



Radiation, Microsolvation, and Low-Temperatures – The Right Balance for the Evolution of Complex Organics in the Universe

Murthy S. Gudipati

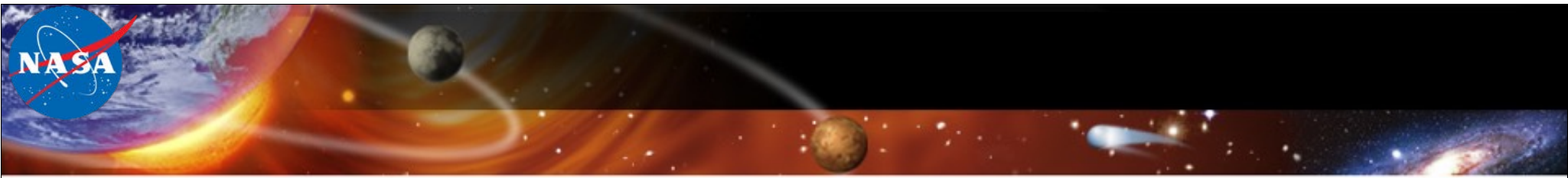
*Jet Propulsion Laboratory, California Institute of Technology,
Pasadena, CA 91109*



Solvation:
The ability of a “medium” to
“assimilate/incorporate” dissimilar components!

Example: NaCl in H₂O (liquid)

Neither Components “Lose Their Identity”

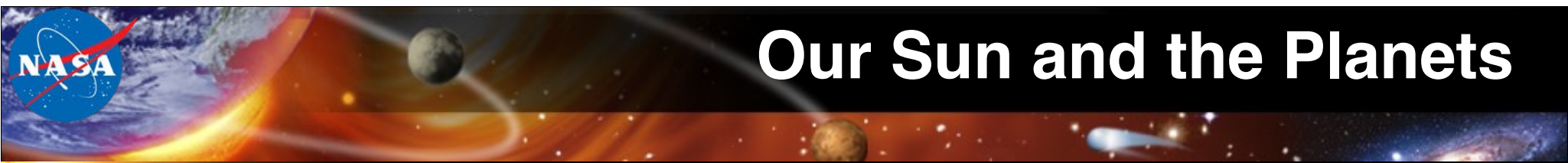


Why?

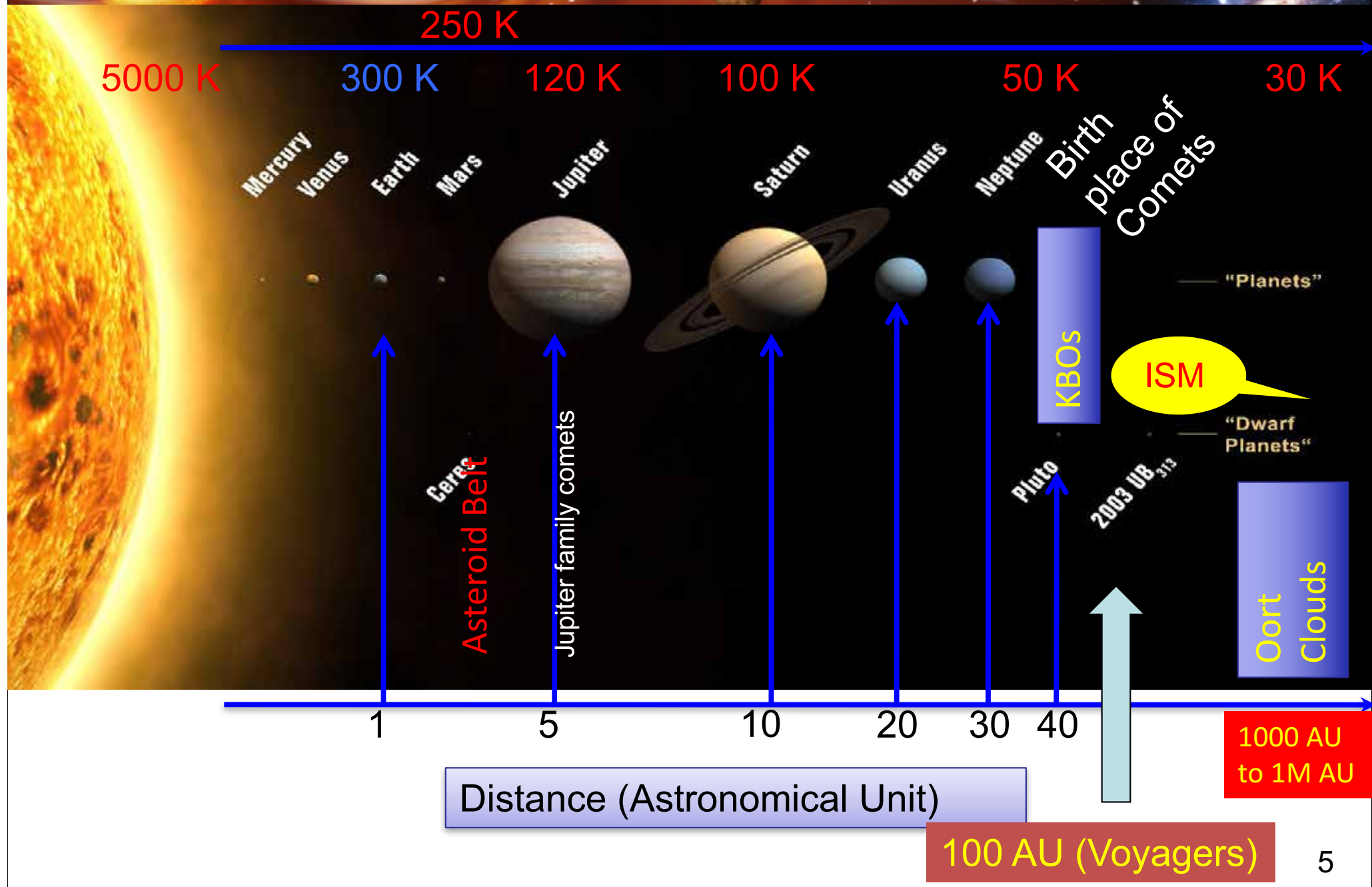


Life on the Blue Dot – Planet Earth





Our Sun and the Planets





Our Galaxy and the Sun

Light Year (LY):

$9.4605284 \times 10^{15} \text{ m}$

63,067 ($\sim 6 \times 10^4$) AU

Astronomical Unit (AU):

$1.49597870691 \times 10^{11} \text{ m}$

Our Galaxy:

10^5 LY diameter

10^3 LY thick (stars)

10^4 LY thick (gas)

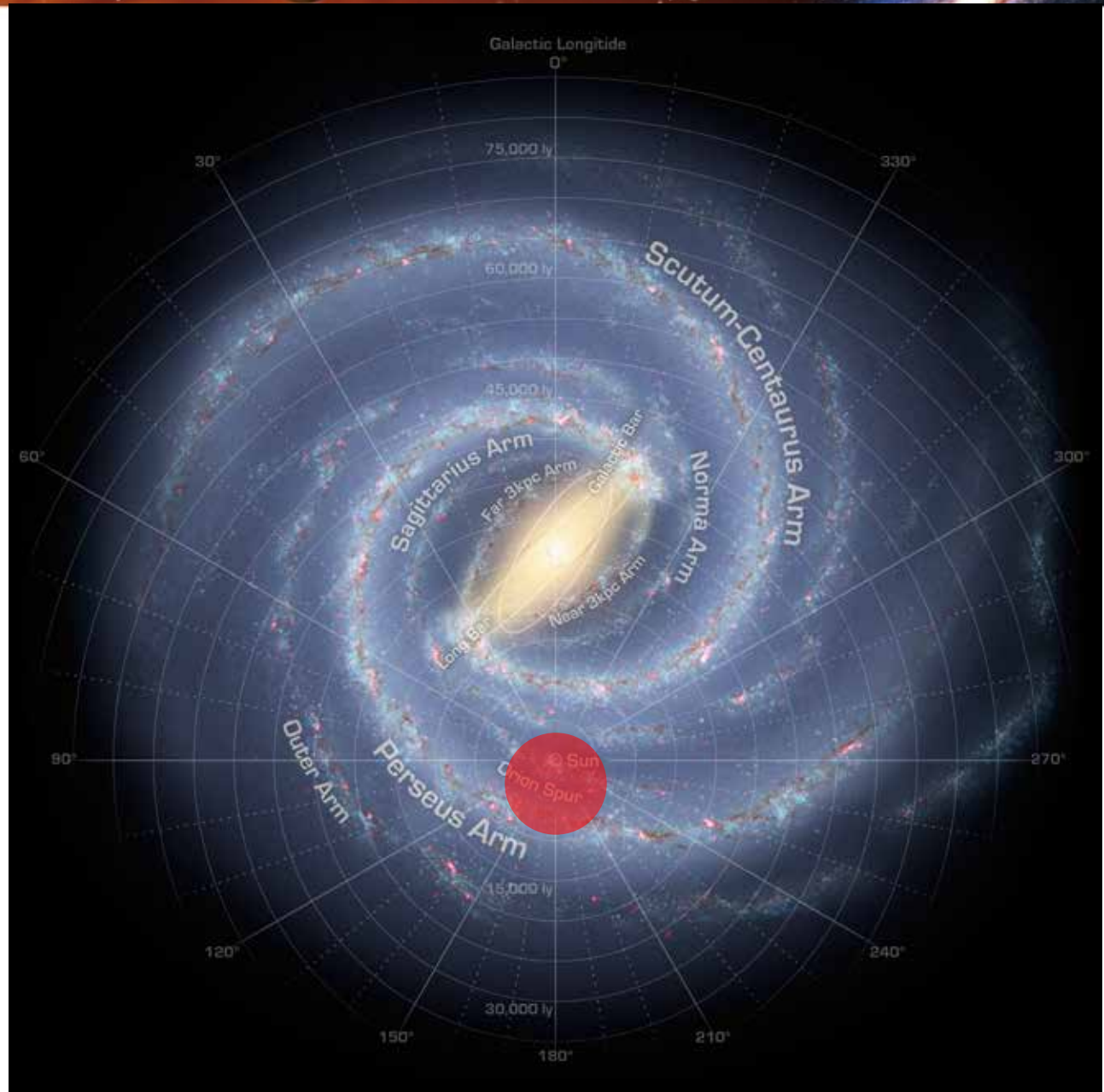
Contains:

2 to 4 $\times 10^{11}$ stars

Next Neighbor:

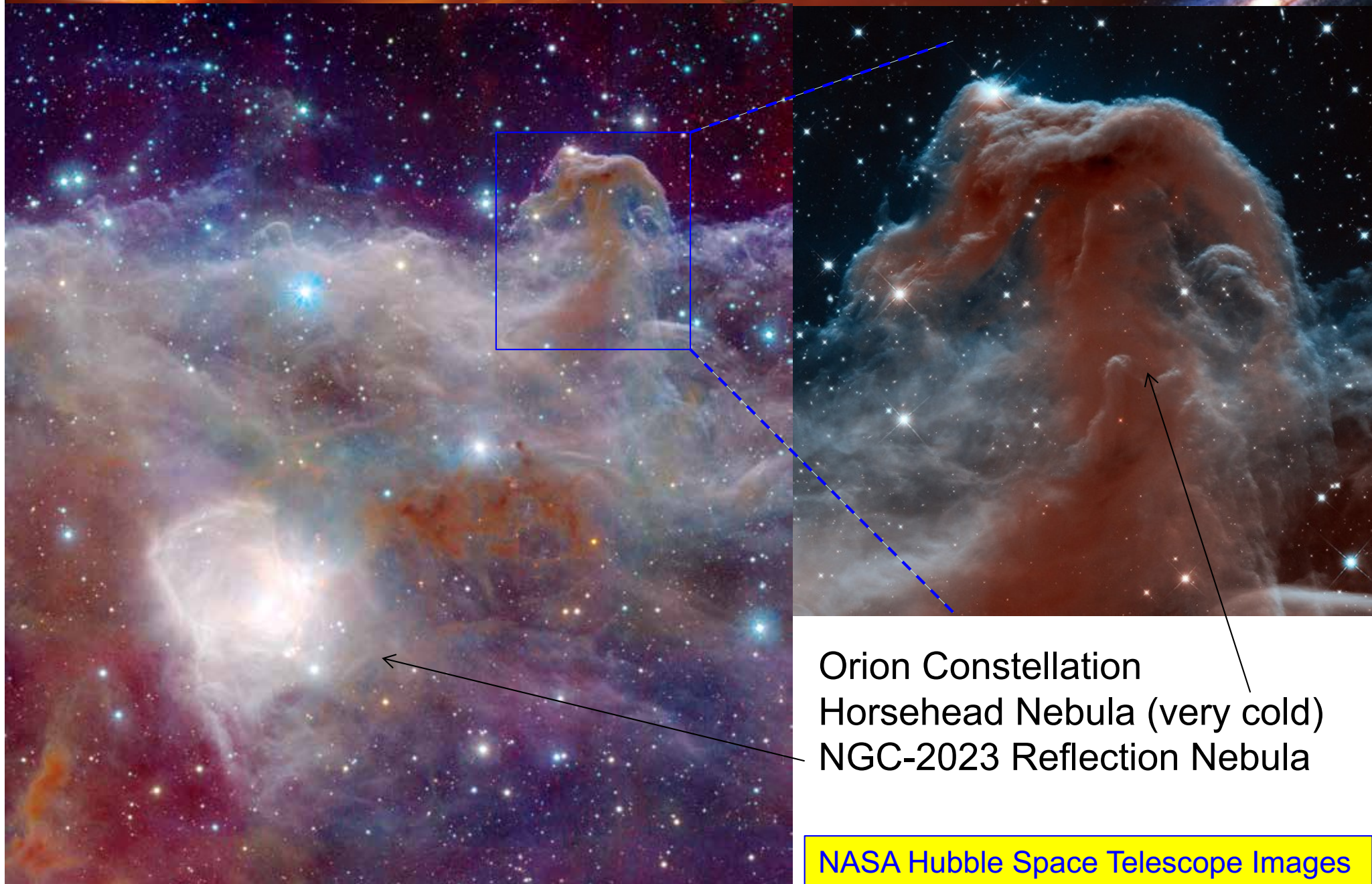
Closest Star ~ 4 LY away

Closest galaxy 2×10^6 LY away





Interstellar Molecular Clouds: Birthplaces for New Stars

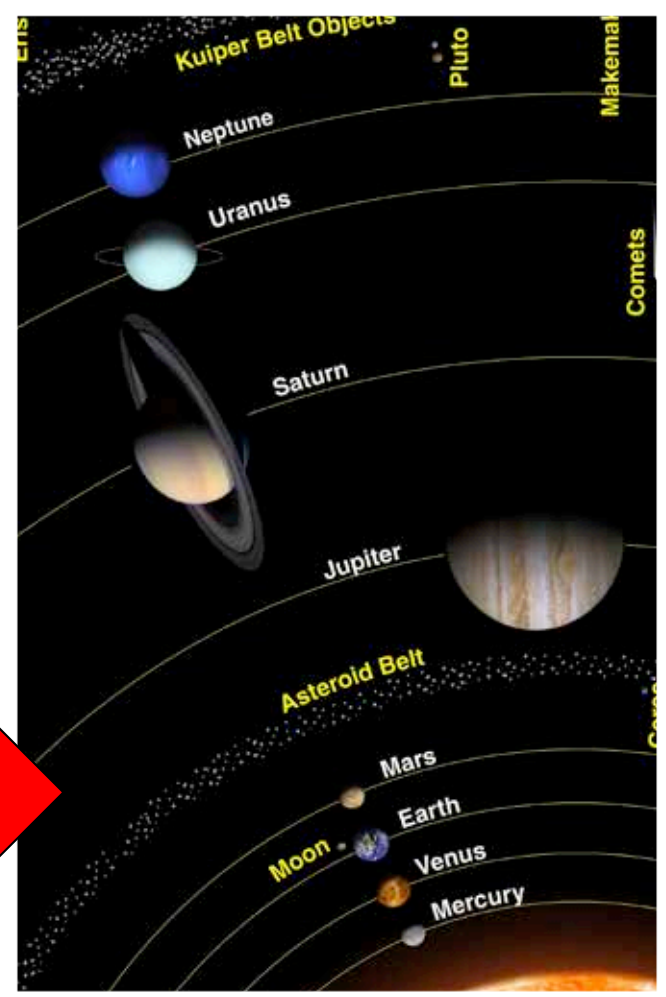
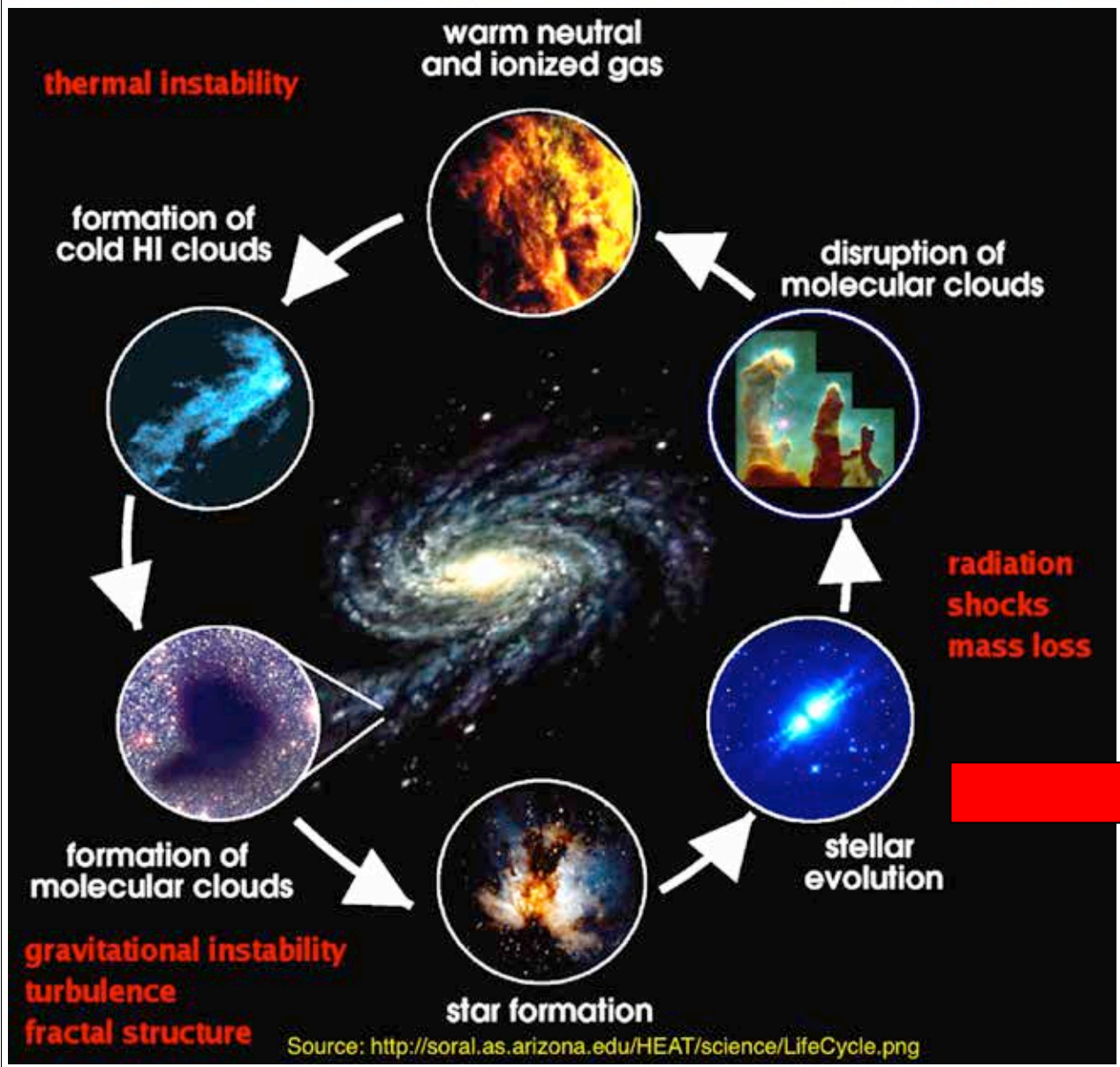


Orion Constellation
Horsehead Nebula (very cold)
NGC-2023 Reflection Nebula

NASA Hubble Space Telescope Images

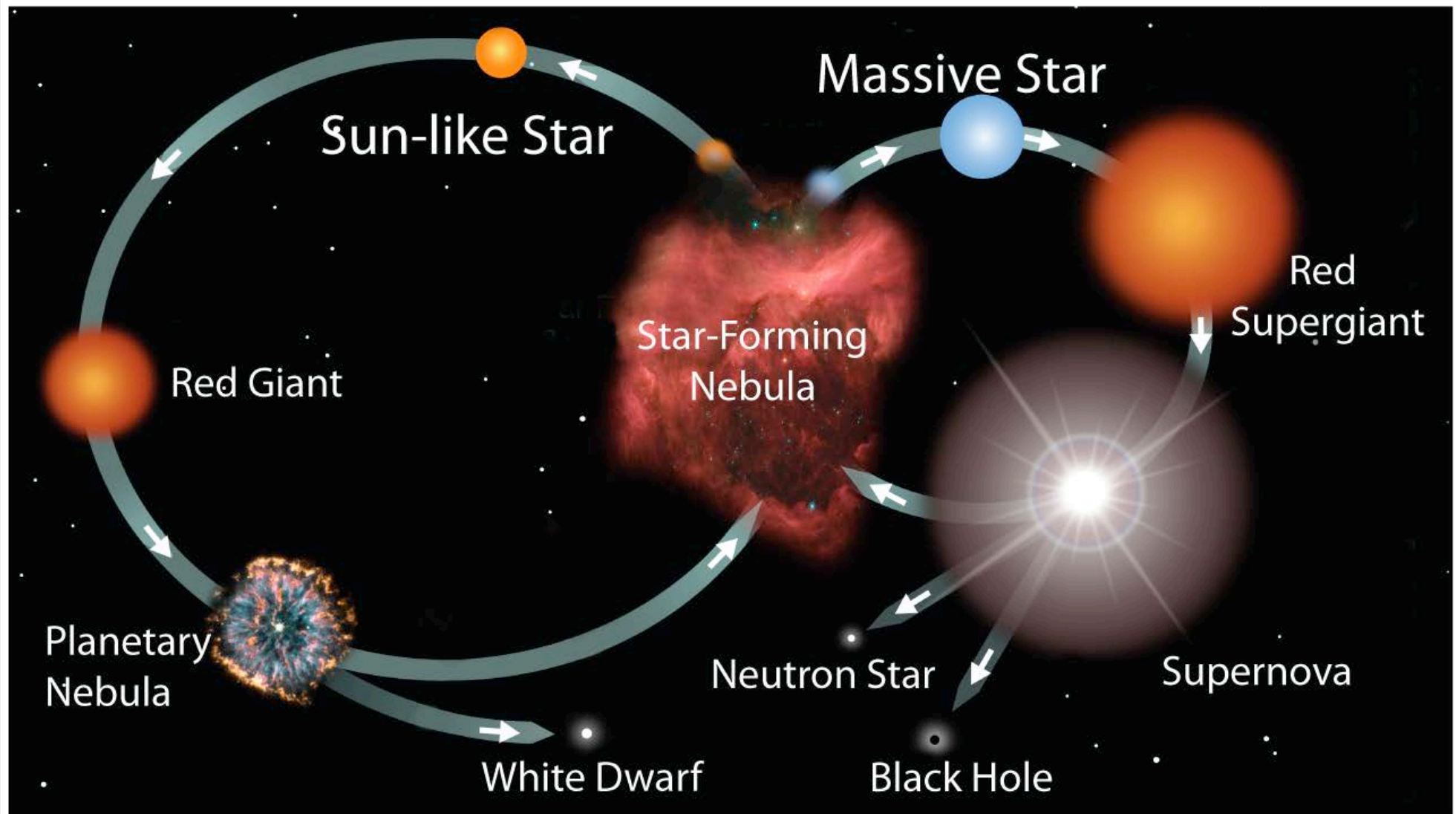


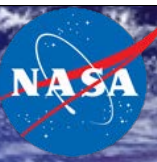
The Lifecycle of a Star





Recycling of Matter: Star Size vs. Its Fate





Composition of Interstellar Medium

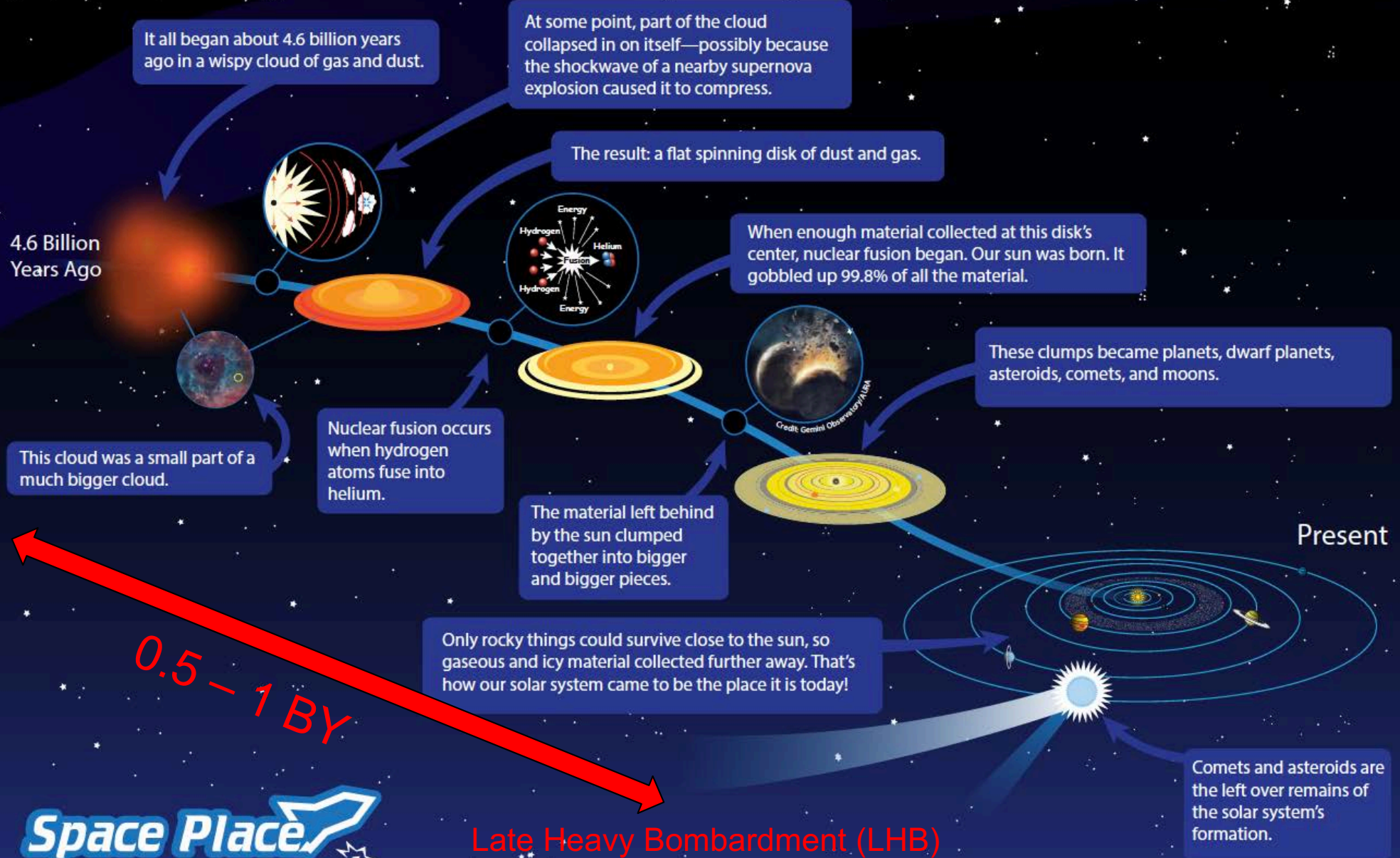
Characteristics of interstellar regions

Region	State of Hydrogen	Other Notable Constituents	Temperature T (K)	Density n (cm ⁻³)
Coronal gas ≈ 50% of ISM by volume	H ⁺	O ⁵⁺	10 ⁵ – 10 ⁶	~ 0.01
Diffuse nebulae (H II regions)	H ⁺	other ions	~ 10 ⁴	10 ² – 10 ³
Intercloud medium ≈ 40% of ISM by volume	H	C ⁺	~ 10 ⁴	~ 0.1
Diffuse clouds	H, H ₂	C ⁺ , CO	50 – 100	10 – 10 ²
Dark clouds (molecular clouds)	H ₂	many molecules	10 – 50	10 ³ – 10 ⁷
Giant molecular clouds ~ 10 ⁵ solar masses	H ₂	CO	~ 10	~ 600

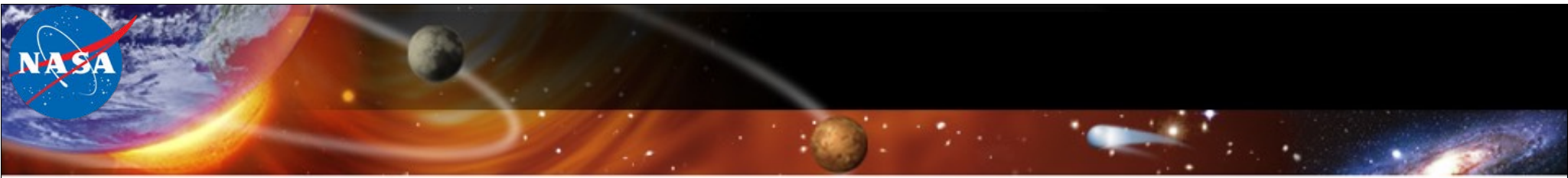
At 1 atm. ~3 x 10¹⁹ molecules / cm³

How did our solar system come to be?

National Aeronautics and
Space Administration



Space Place
in a Snap!



Water



Elemental Abundance of Our Galaxy (excluding Dark Matter/Dark Energy)

Most abundant molecules in the Universe are:

H_2 (Hydrogen)

H_3^+ (Trihydrogen)

H_2O (Water)

C_nH_m (Hydrocarbons)

NH_3 (Ammonia);

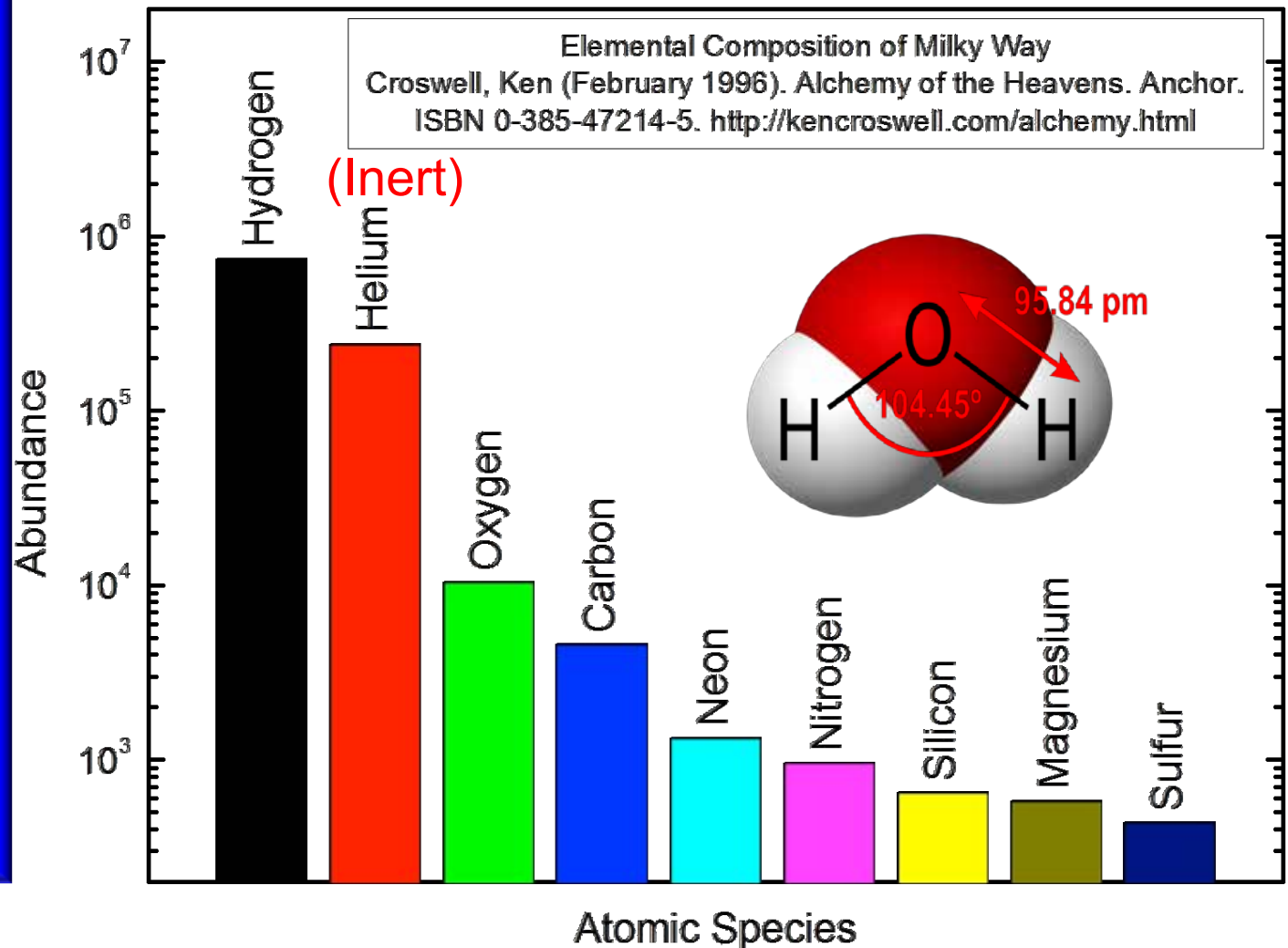
O_2 (Oxygen);

CO (Carbon Monoxide)

CO_2 (Carbon Dioxide)

N_2 (Nitrogen)

etc...

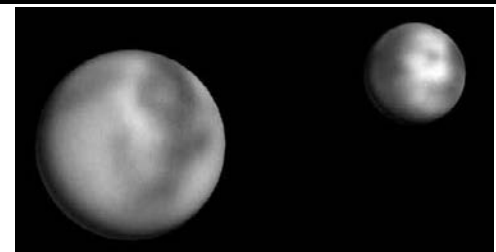
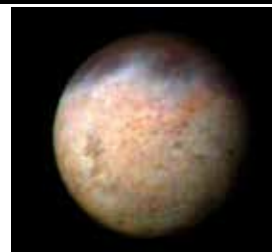


H_2O is the most abundant triatomic molecule based on cosmic elemental abundance, followed by hydrocarbons.

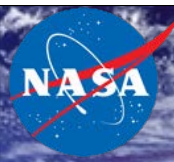


Icy Satellites of Outer Planets

Ices and Other Surface Materials	
Jovian satellites	
Io	SO_2 , SO_3 , H_2S ?, H_2O ?
Europa	H_2O , SO_2 , SH , CO_2 , CH_4 , X , $\text{X}=\text{CN}$, hydrated sulfate and carbonate minerals, H_2O , H_2SO_4
Ganymede	H_2O , SO_2 , SH , CO_2 , CH_4 , X , $\text{X}=\text{CN}$, hydrated and hydroxylated minerals, O_2 , O_3
Callisto	H_2O , SO_2 , SH , CO_2 , CH_4 , $\text{X}=\text{CN}$, hydrated and hydroxylated minerals
Saturnian satellites	
Mimas	H_2O
Enceladus	H_2O
Tethys	H_2O
Dione	H_2O , C , HC , O ,
Rhea	H_2O , HC ?, O ,
Hyperion	H_2O
Iapetus	H_2O , C , HC , H_2S ?
Phoebe	H_2O
Rings	H_2O
Uranian satellites	
Miranda	H_2O , NH_3 , hydrate, hydroxylated silicates
Ariel	H_2O , OH ?
Umbriel	H_2O
Titania	H_2O , C , HC , OH ?
Oberon	H_2O , C , HC , OH ?
Neptunian satellites	
Triton	N_2 , CH_4 , CO , CO_2 , H_2O
Pluto	N_2 , CH_4 , CO , H_2O
Charon	H_2O , NH_3 , NH_4 , hydrate
Trans-Neptune objects	
	H_2O , HC ices (e.g., CH_4 , C_2H_6 , OH), HC , silicates

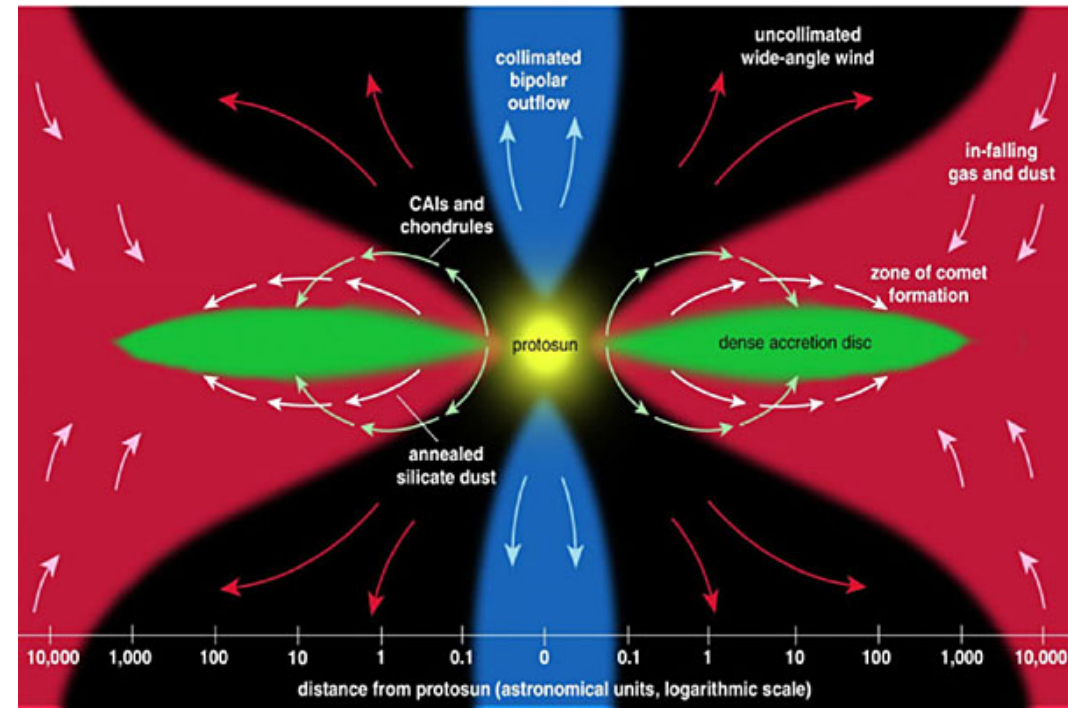
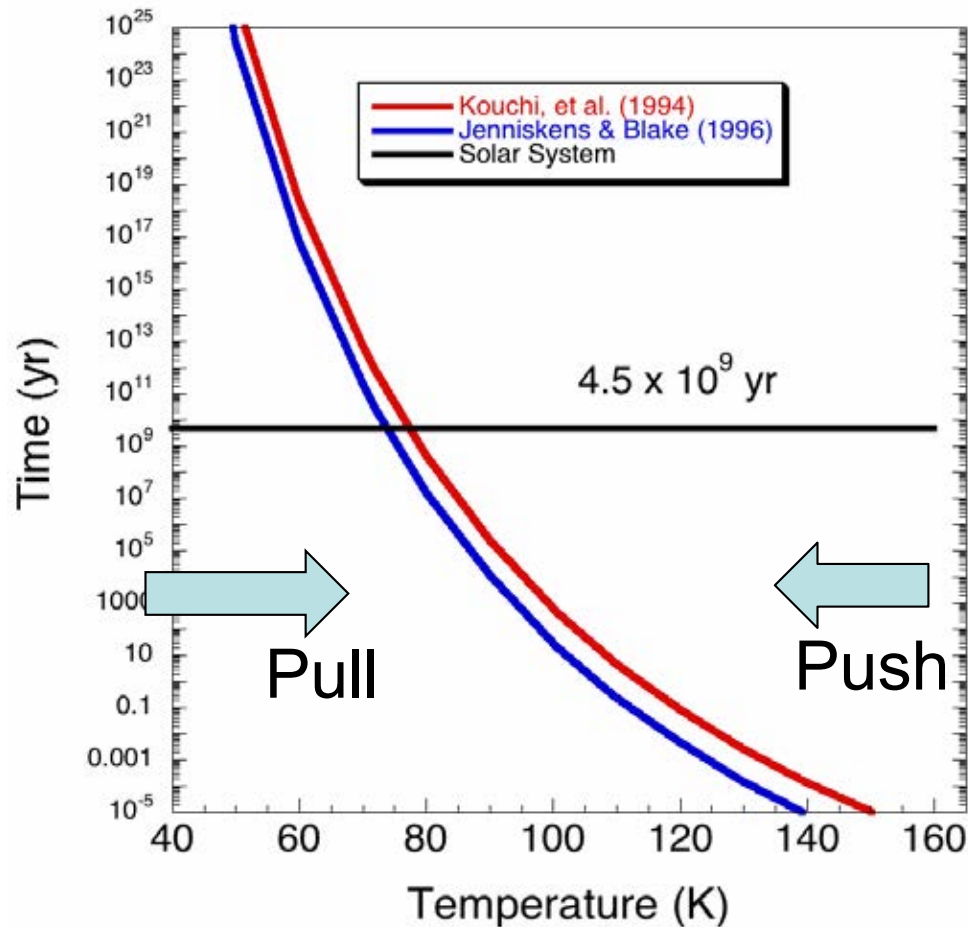


Ted Roush, JGR E12, **106**, 33315 (2001)



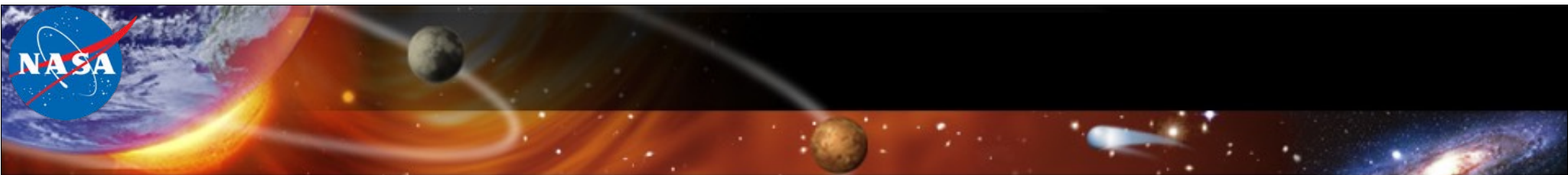
Cometisimals to Comets – Push or Pull?

The Cometary Mystery of Protoplanetary Disk



(from Nuth, J. A., 2001, *American Scientist*, v. 89, p.230.)

Mastrapa, Grundy, Gudipati (Solar System Ices 2013)

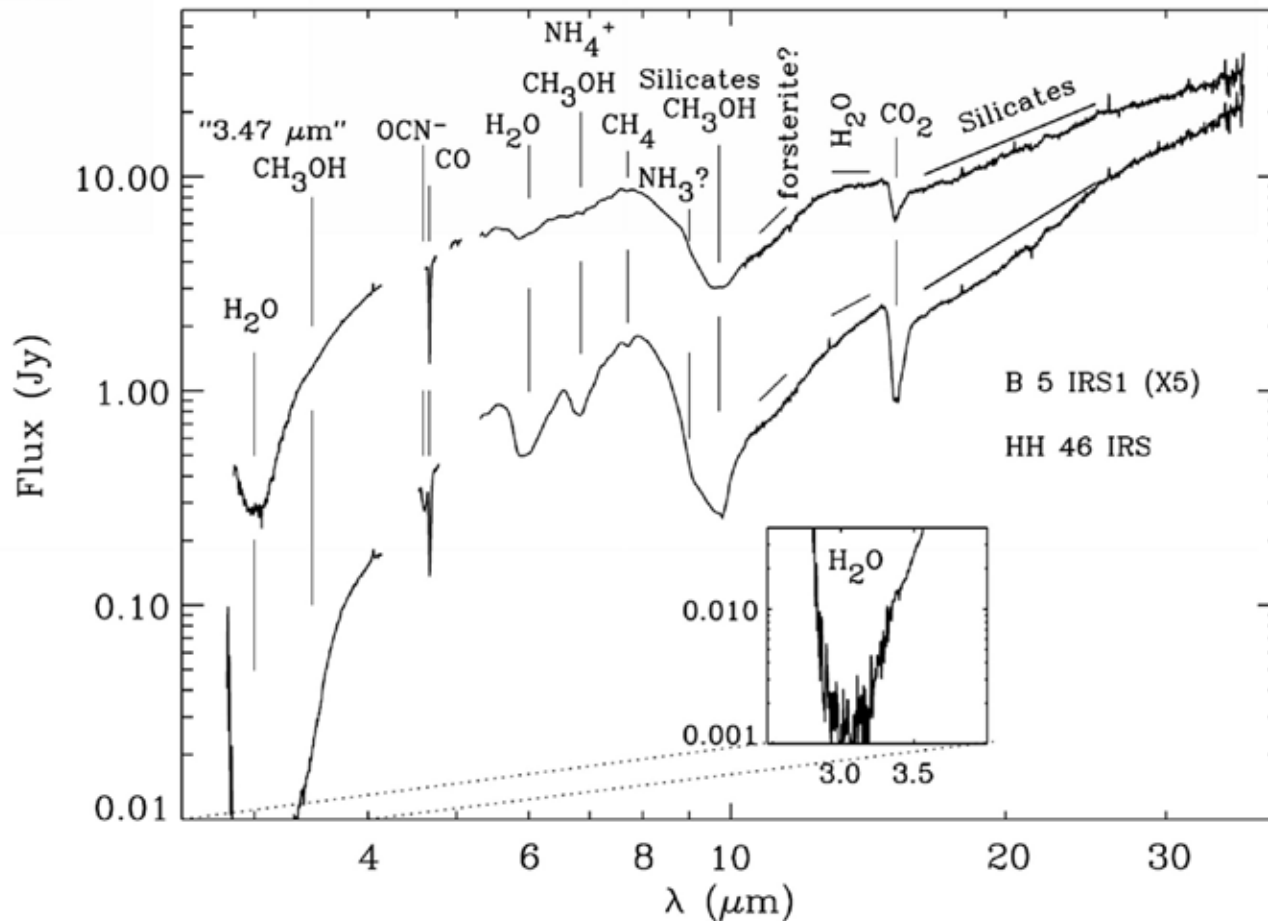


Organics

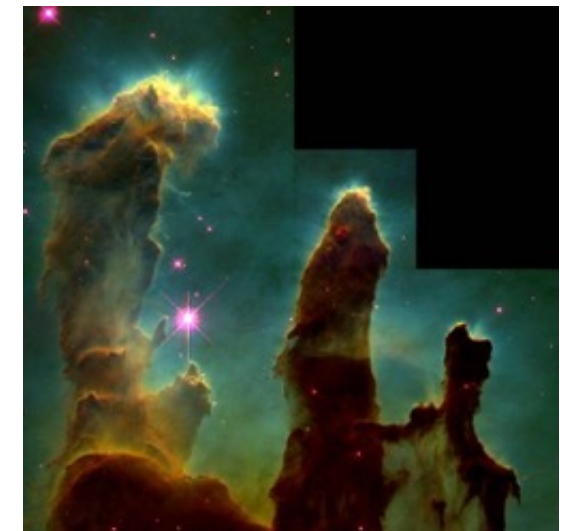
NASA Interstellar Ice Grains: Loaded with Organics

Amorphous Interstellar Ices

BOOGERT ET AL.



Star-forming Regions /
Protostars



Dense Molecular Clouds
(The Eagle Nebulae)

Oort Cloud Comets – Similar Composition?



How many of you have seen a comet?

Hale-Bopp



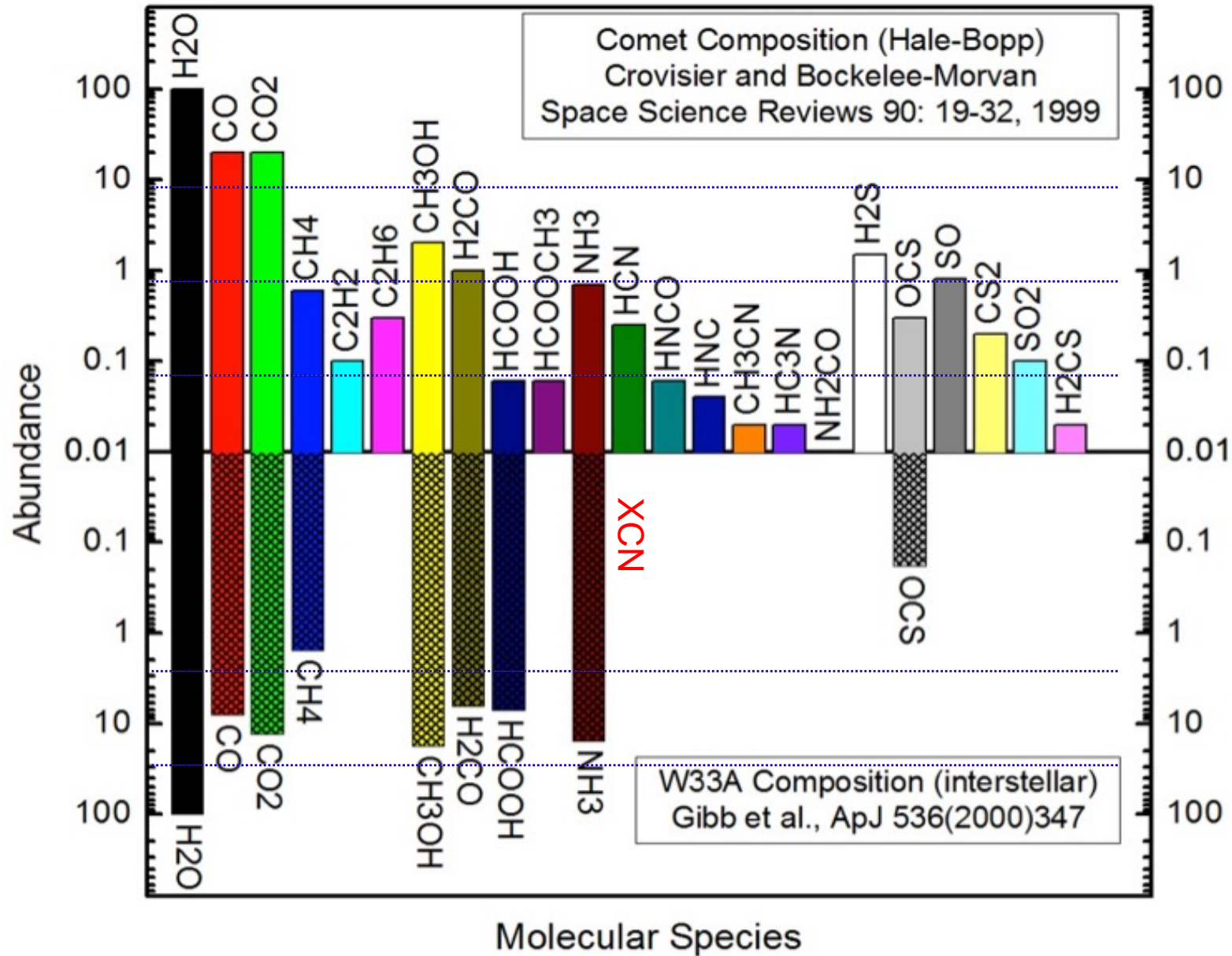
Hale-Bopp
Taken 2/20/97 with Red Back Sanyo Park
Celestron Epoch 8" f/5 Schmidt camera
© 1997 Luke Kim Tan



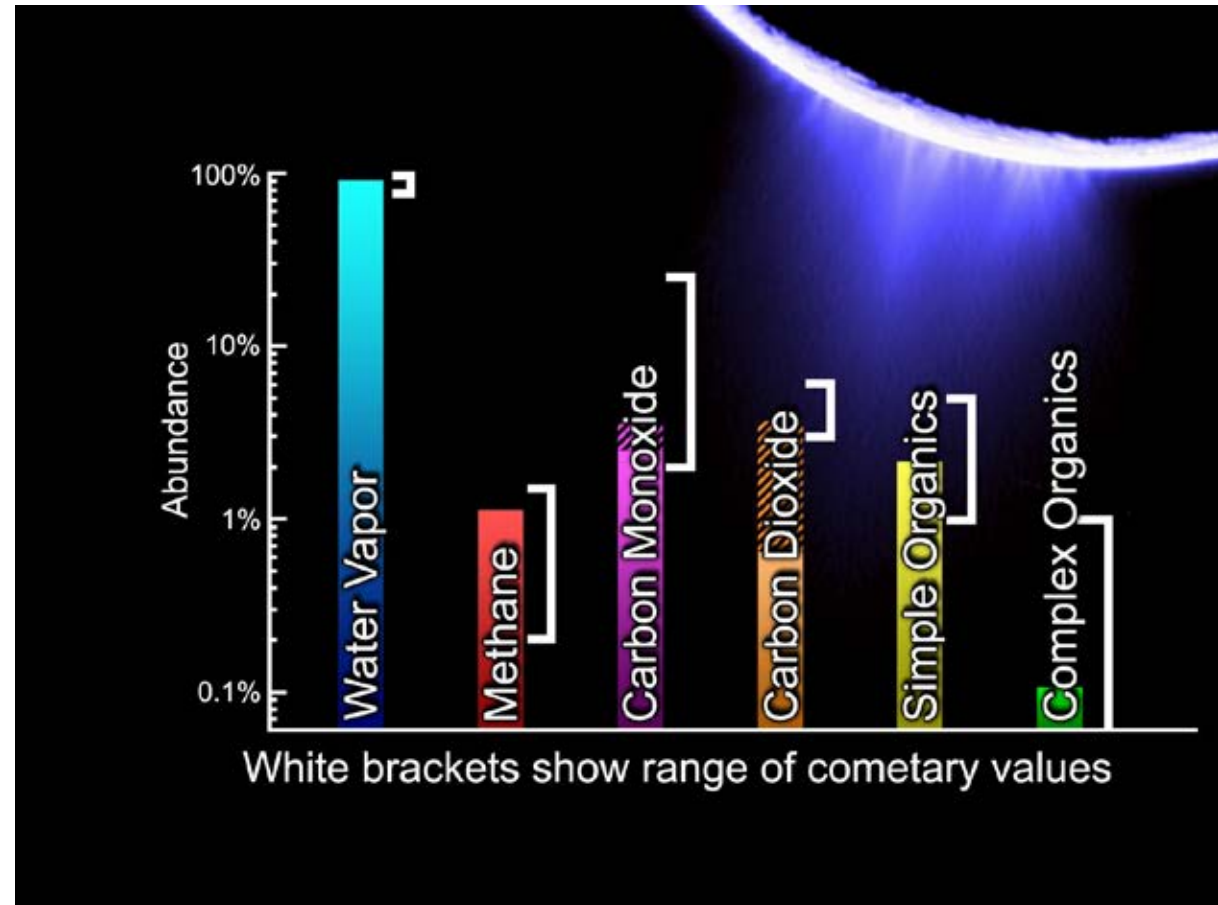
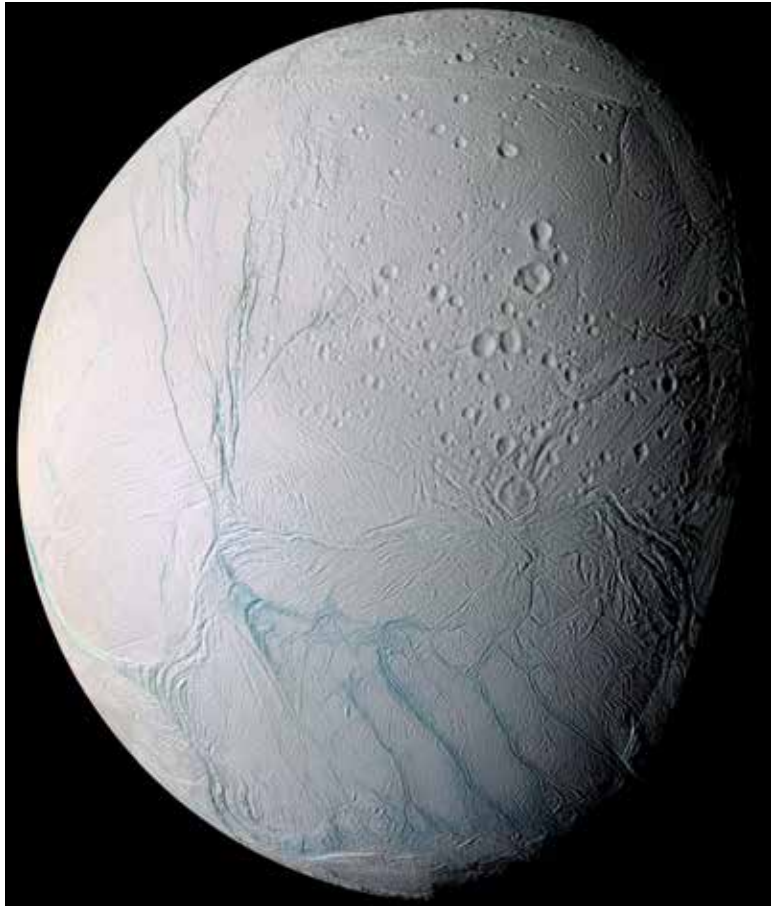
McNaught



Similar Composition: Comets and Interstellar Ice Grains



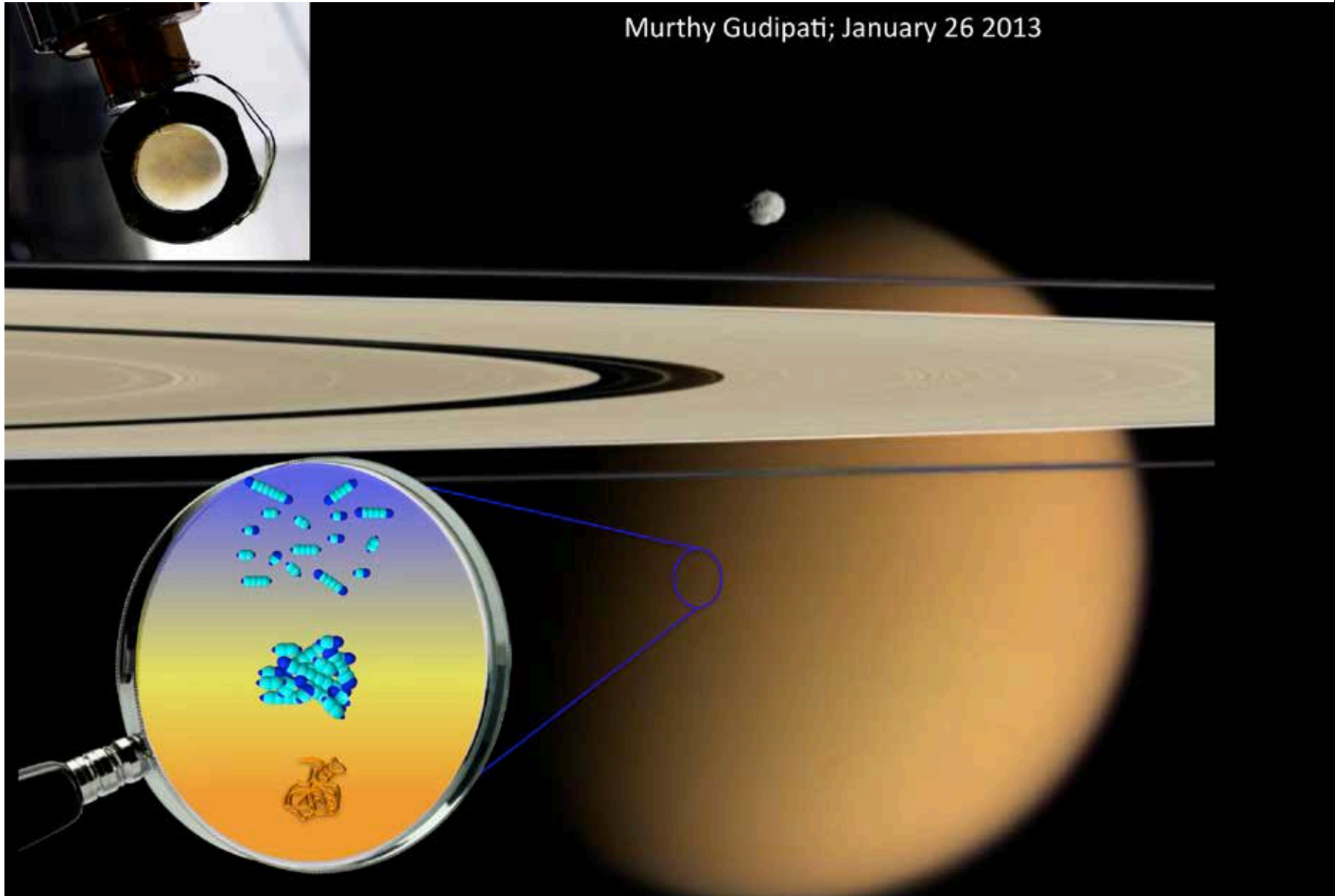
Enceladus (Saturn's Icy Moon) Plumes

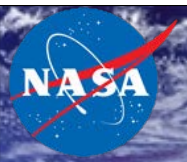


NASA Cassini Mission



Murthy Gudipati; January 26 2013

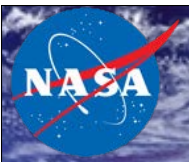




Titan Subsurface Oceans: Habitable?

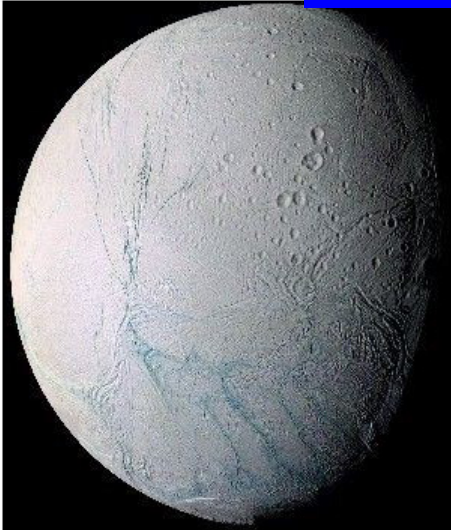
If this Titan's surface boulder were to be water-ice coated with organic solid and exposed to >350 nm solar photons, then building blocks of life would be formed here and transported into the interior water oceans – a habitable environment.



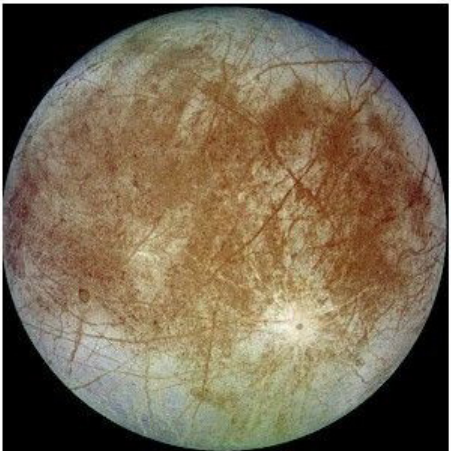


Ice Spectroscopy Lab @ JPL

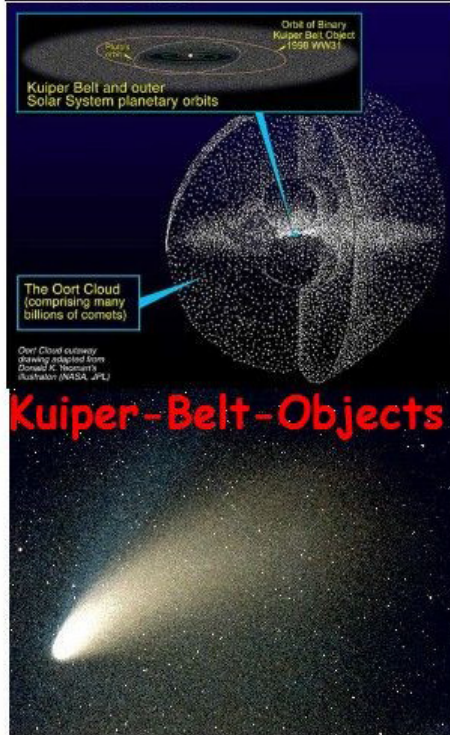
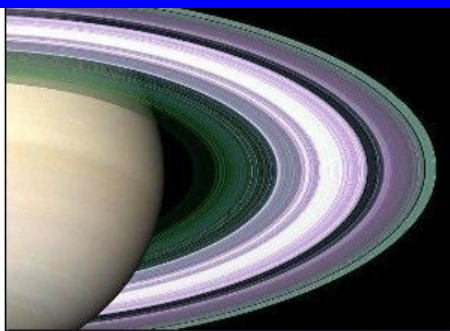
Our research spans many icy bodies
(including Titan, not shown here)
in the solar system and interstellar medium



Enceladus



Europa



Kuiper-Belt-Objects

Comets (Hale-Bopp)



Galactic (Milky Way)

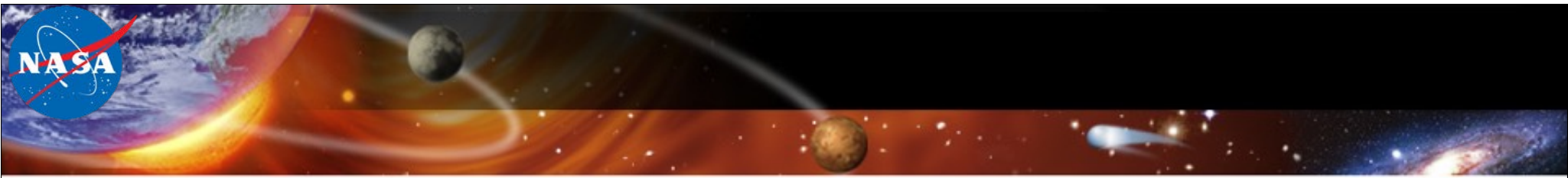


Horse-Head Nebula

Interstellar Medium Dense Molecular Clouds



NGC-7331 Twin of the Milky Way



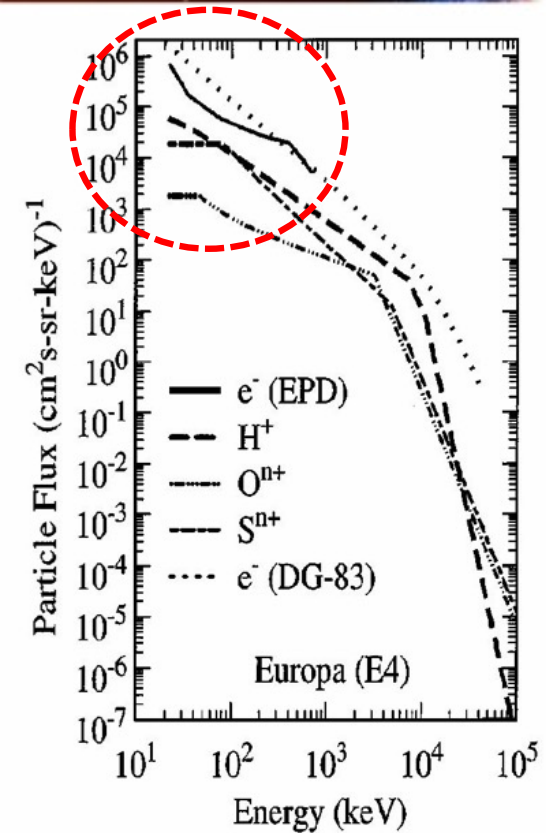
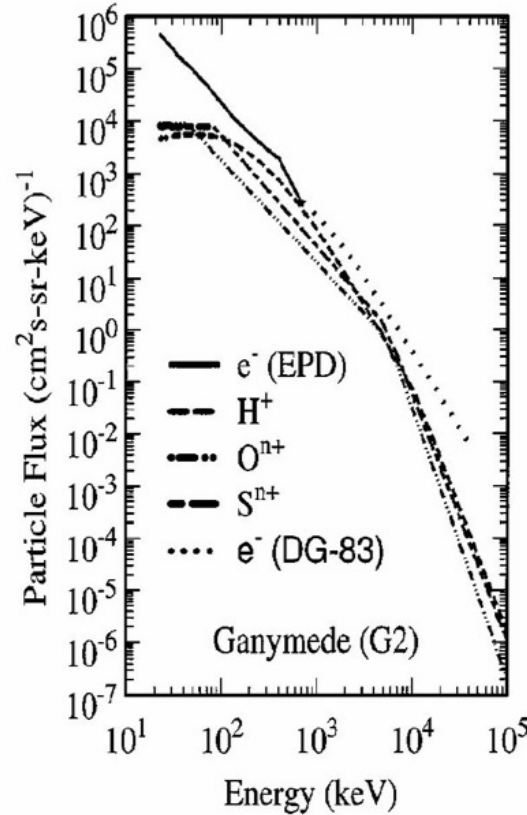
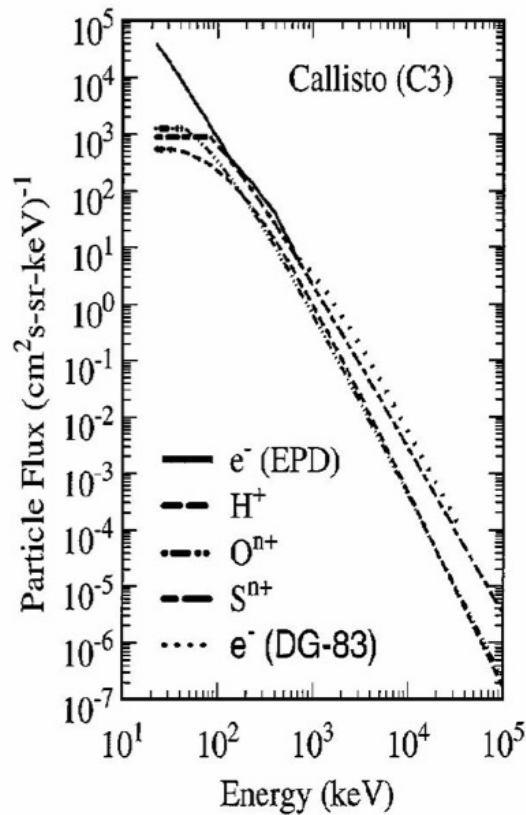
Radiation



Europa's Radiation Environment

Q

keV⁻¹



Galileo Orbiter measurements of energetic ions (20 keV to 100 MeV) and electrons (20–700 keV) in Jupiter's magnetosphere are used in conjunction with the JPL electron model (<40 MeV) to compute irradiation effects in the surface layers of Europa, Ganymede, and Callisto.

John Cooper et al. Icarus (2001)



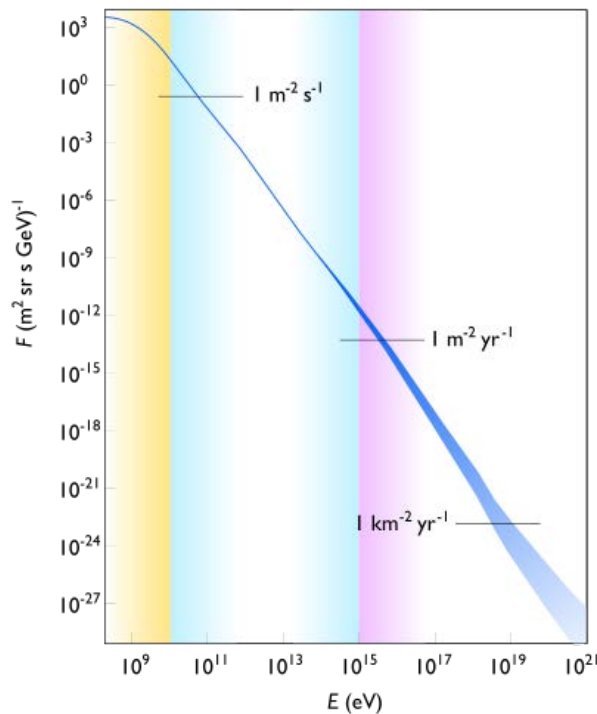
Radiation

High-Energy Radiation (10^{21} - 10 eV)

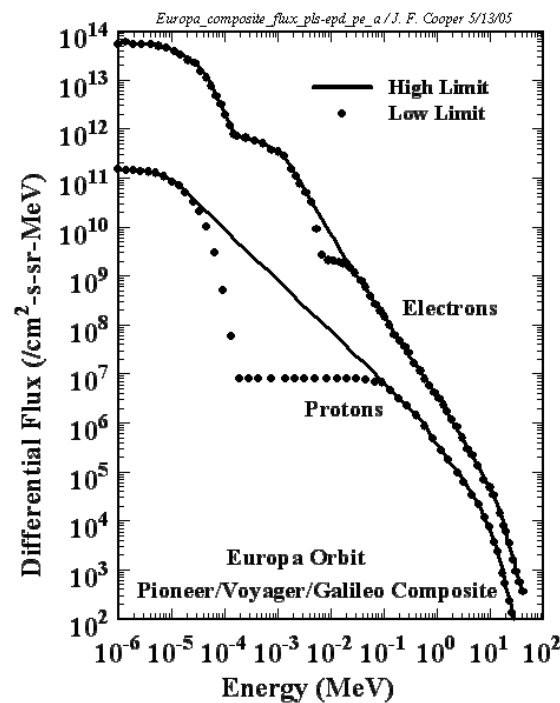
Cosmic Rays (90% protons, 9% are helium nuclei - alpha particles, 1% electrons -beta minus particles), Magnetospheric Electrons, Protons, Ions, γ -Rays, X-Rays, Extreme UV Photons – extreme high energy particles from Galactic Core.

Low-Energy Radiation (<10 eV)

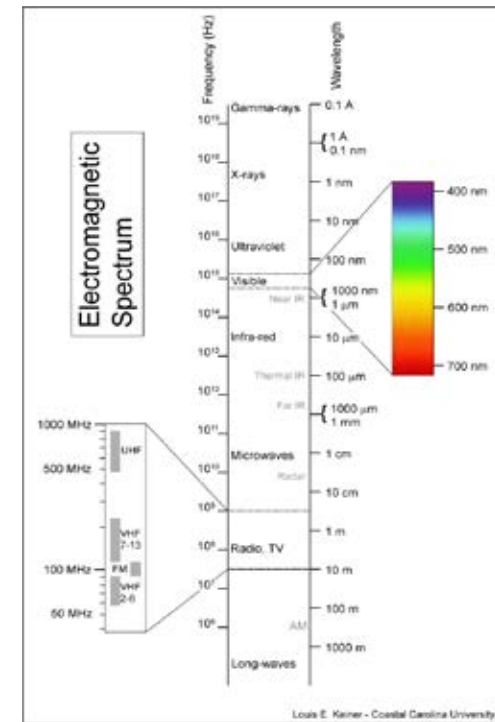
UV-VIS-IR Photons, Slow Electrons, Protons, and Ions



Cosmic Rays



Jupiter's Magnetosphere at Europa



Electromagnetic Spectrum



Radiation Chemistry of Ices

(dissociation & ionization – storage of energy & highly reactive species)

Quanta of Energy deposited in ices to heat, dissociate, and ionize molecules in these ices

Photons (< 20 eV) : a few events

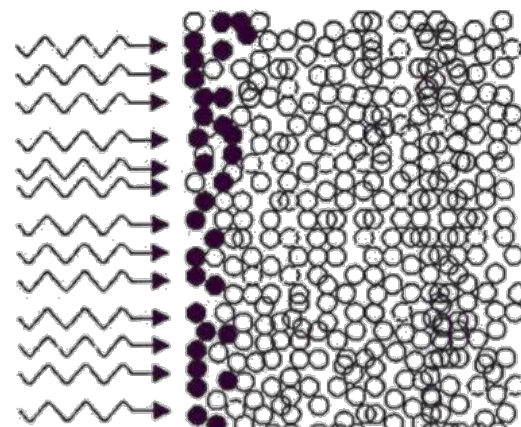
Particles (MeV): 100 to 1000 events

**Photons - few microns
Cosmic Rays ~ meter**

**Energy Storage
Reactive Species
Chemistry**

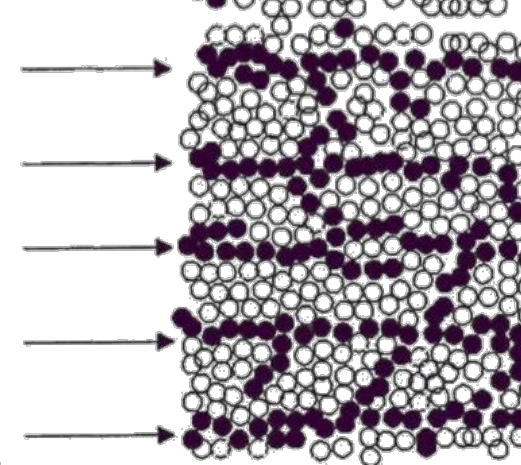
UV Photons

- Break bonds
- Ionize species
- Penetration limited by optical properties of ice



Cosmic Rays (protons)

- Break bonds
- ionize species
- generate high-energy secondary electrons
- penetration limited by energy of particle and stopping power of ice

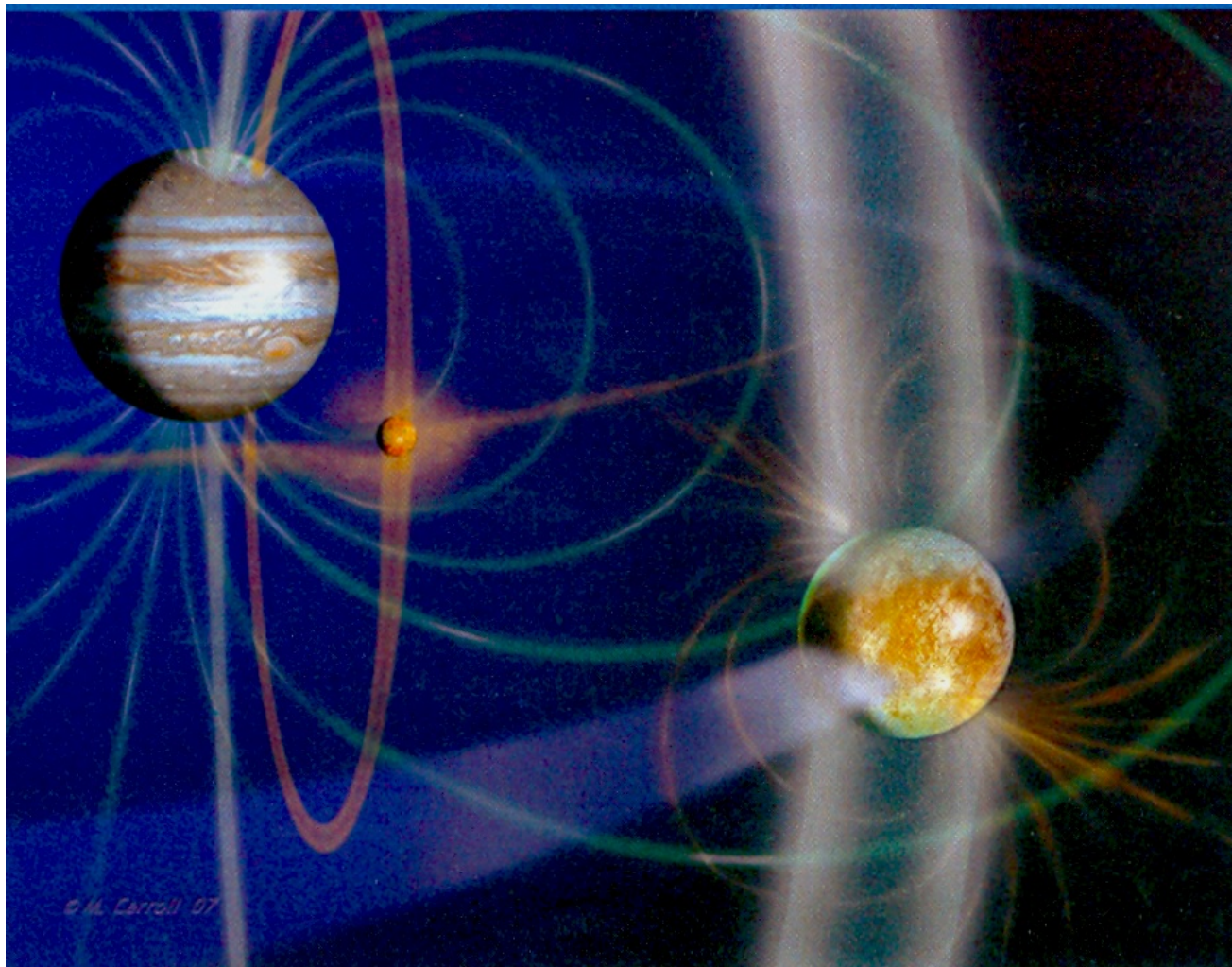


Spinks and Woods: "Introduction to Radiation Chemistry", John Wiley Pub., NY, 1990, p.3

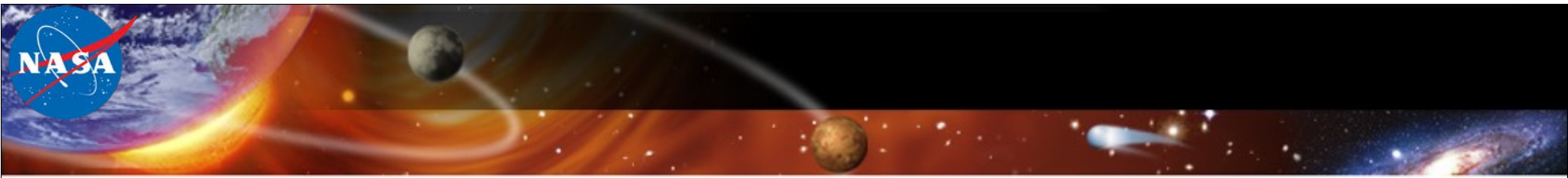


Radiation Environment of Europa - Electrons

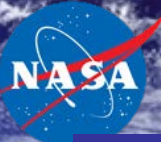
Electrons Reaching Europa's Surface: Trailing (colored) Hemisphere: **<25 MeV**; Leading Hemisphere: **>25 MeV**



Q

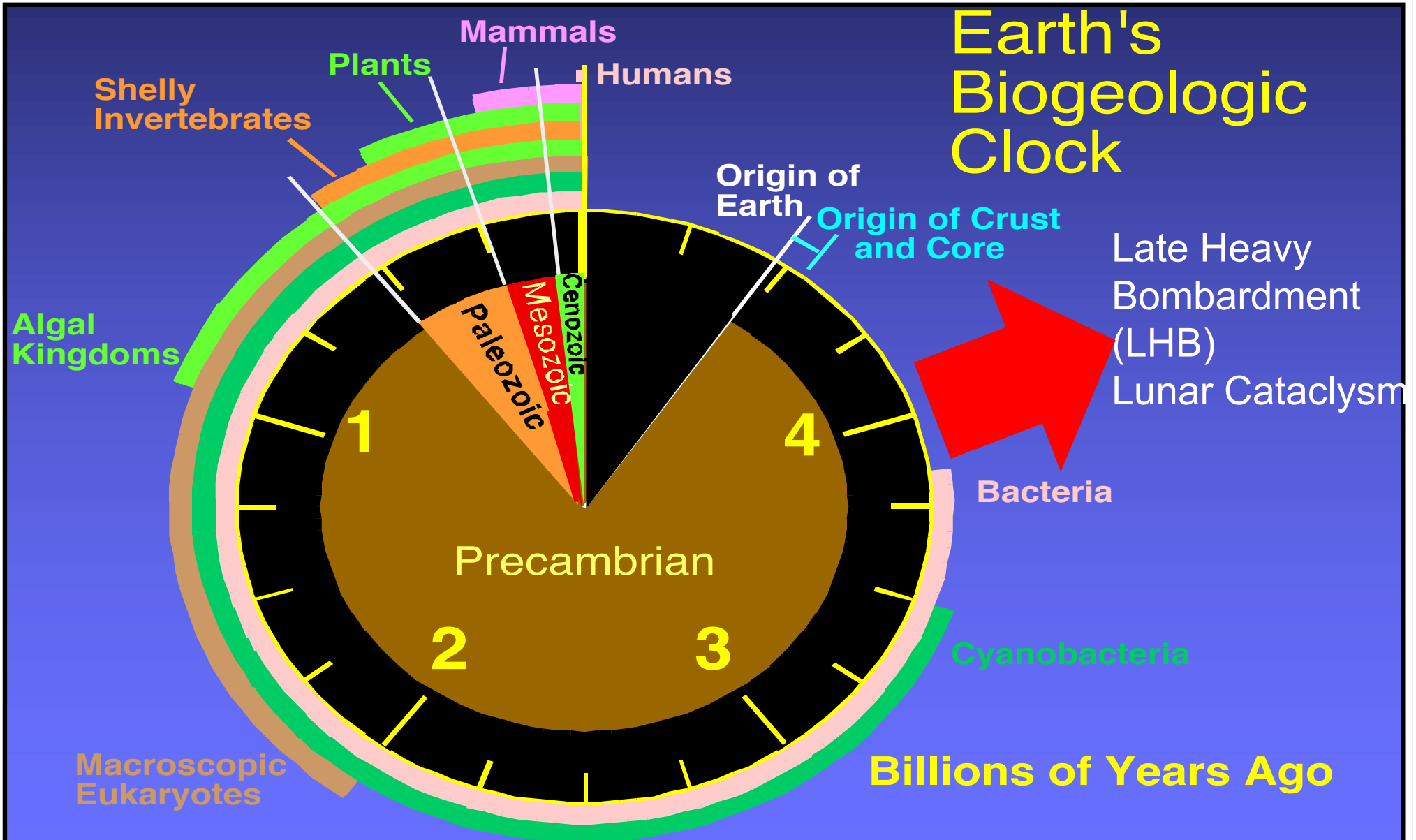


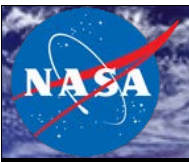
Life On Earth How?



Earth, Comets & Asteroids, and Life

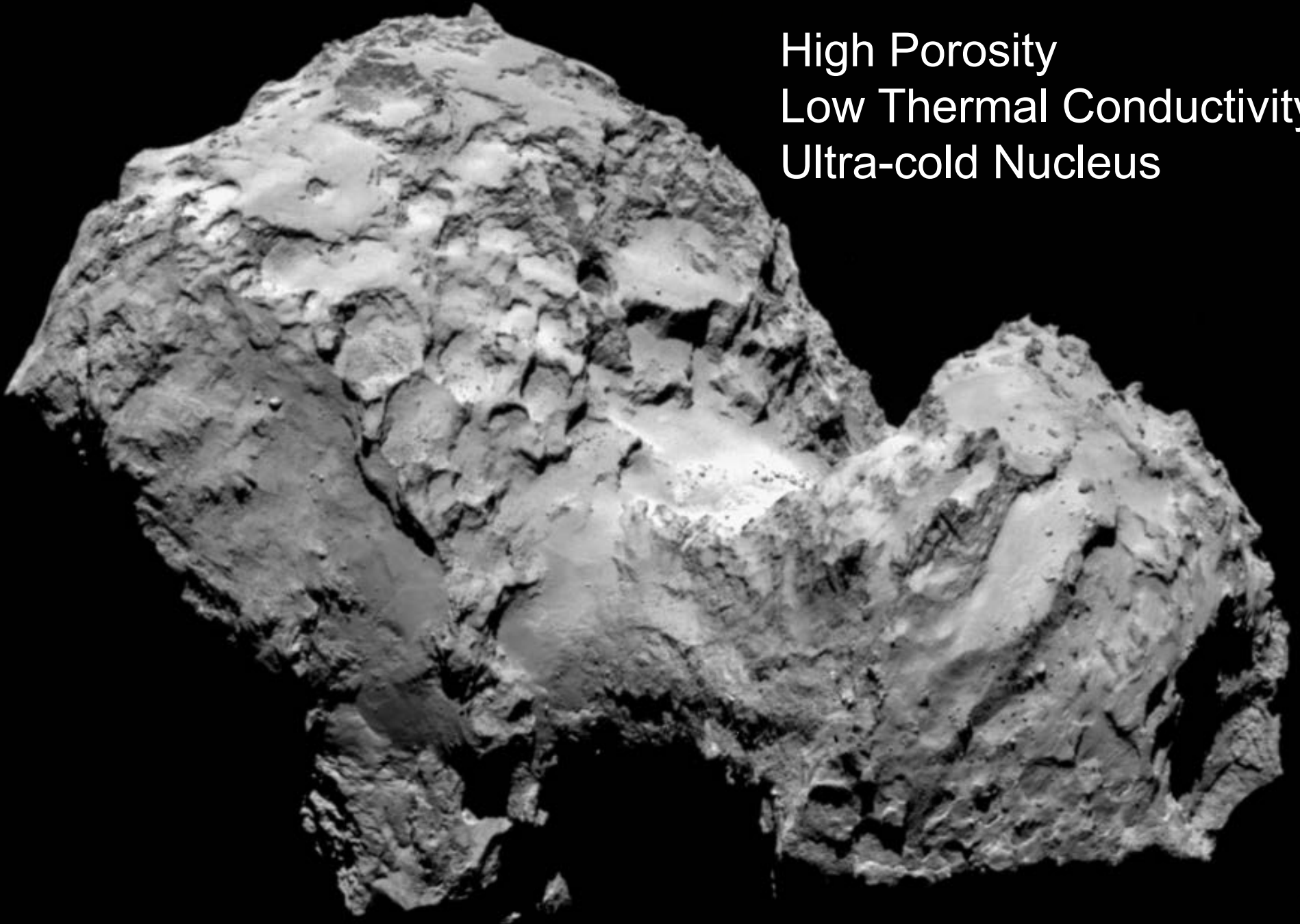
Water & Organic Matter delivered to Earth by Comets/Asteroids ~4 Billion Years Ago

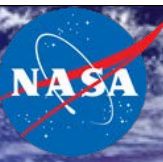




67P/Churyumov-Gerasimenko

High Porosity
Low Thermal Conductivity
Ultra-cold Nucleus





The Origin(s) of Life – Role of Comets

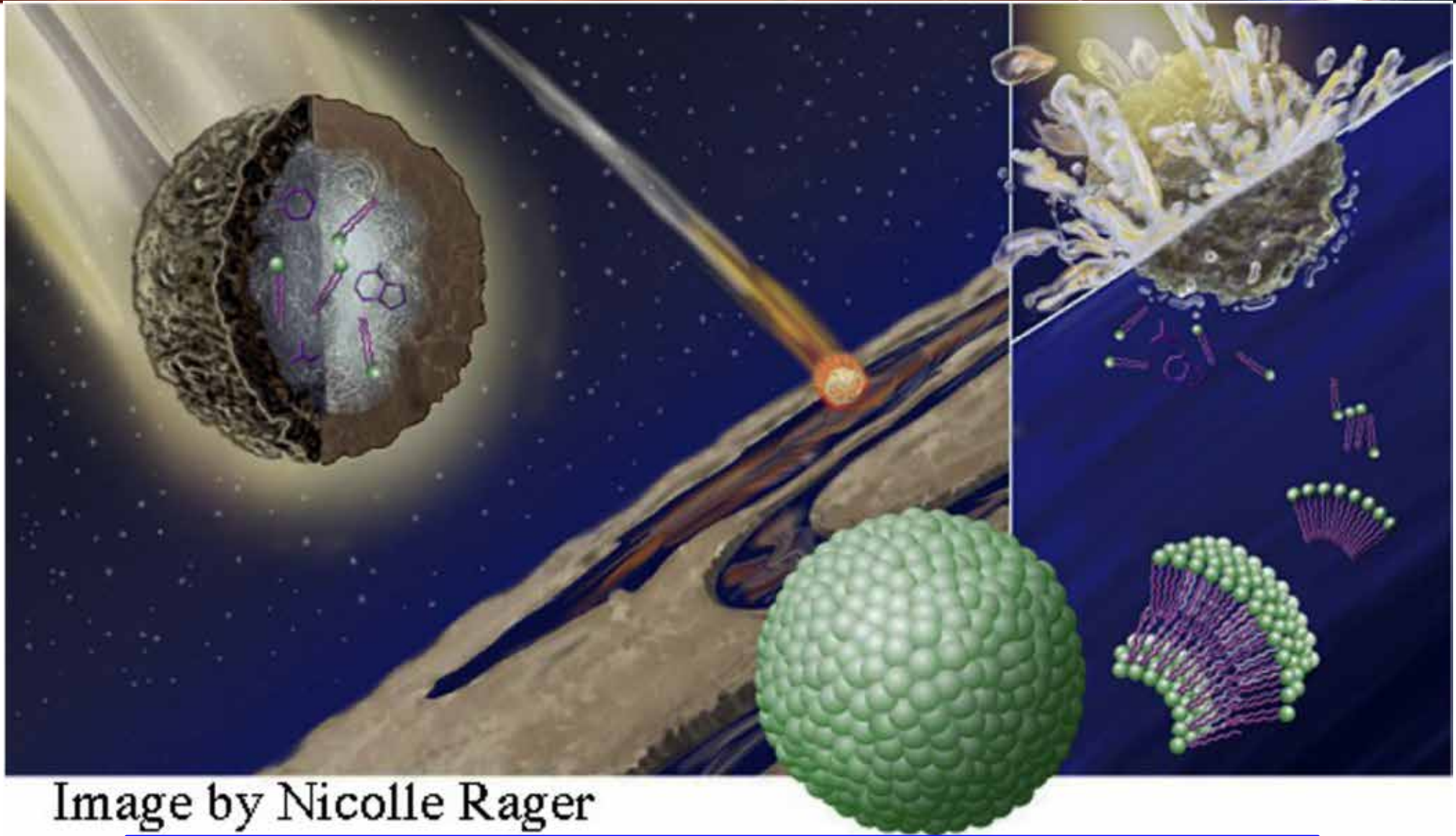
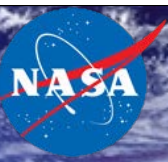
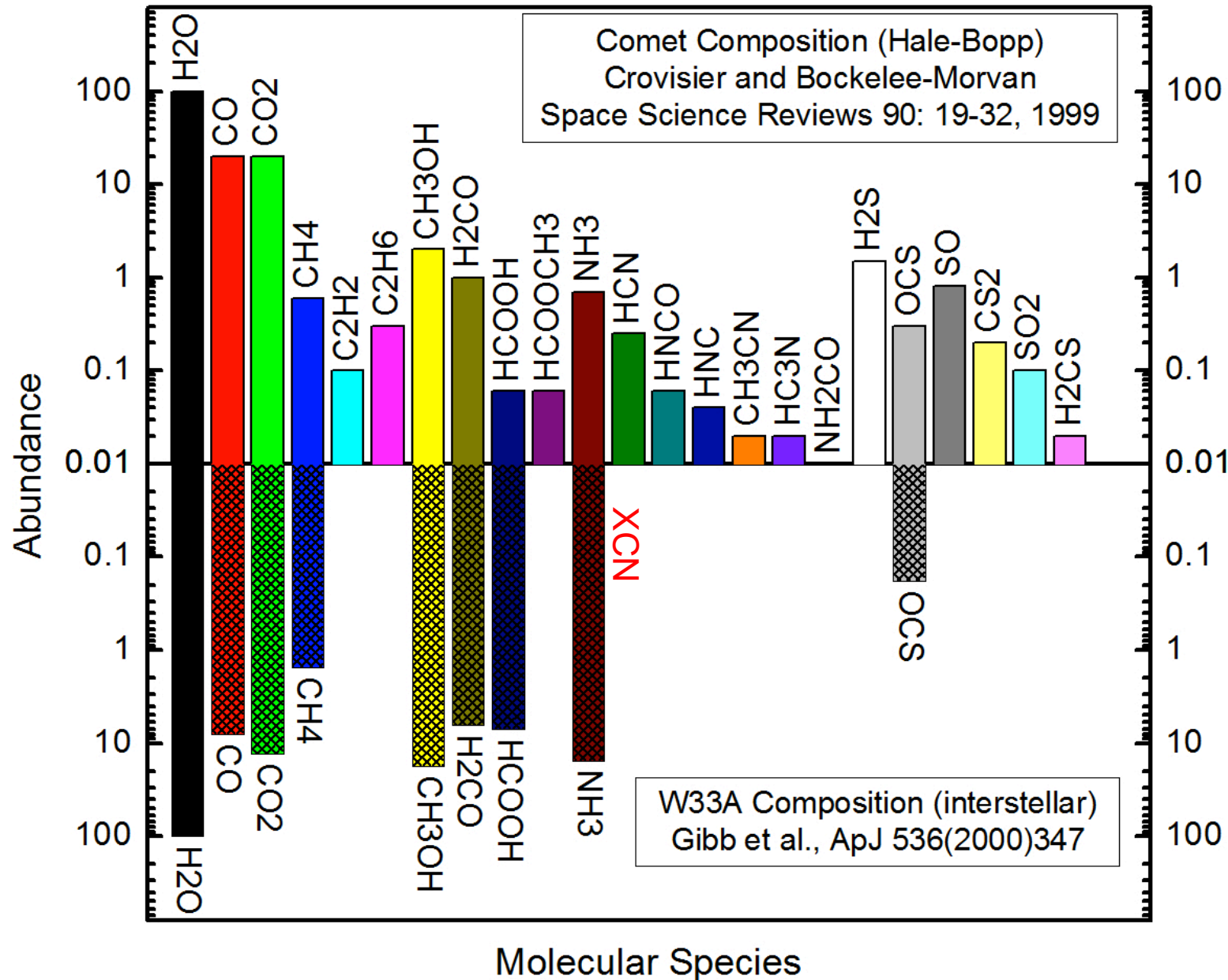


Image by Nicolle Rager

Did Organics Survive Comet Entry and Impacts on Earth?
Do we fully understand Comets? (Deep Impact, Epoxi, Rosetta)

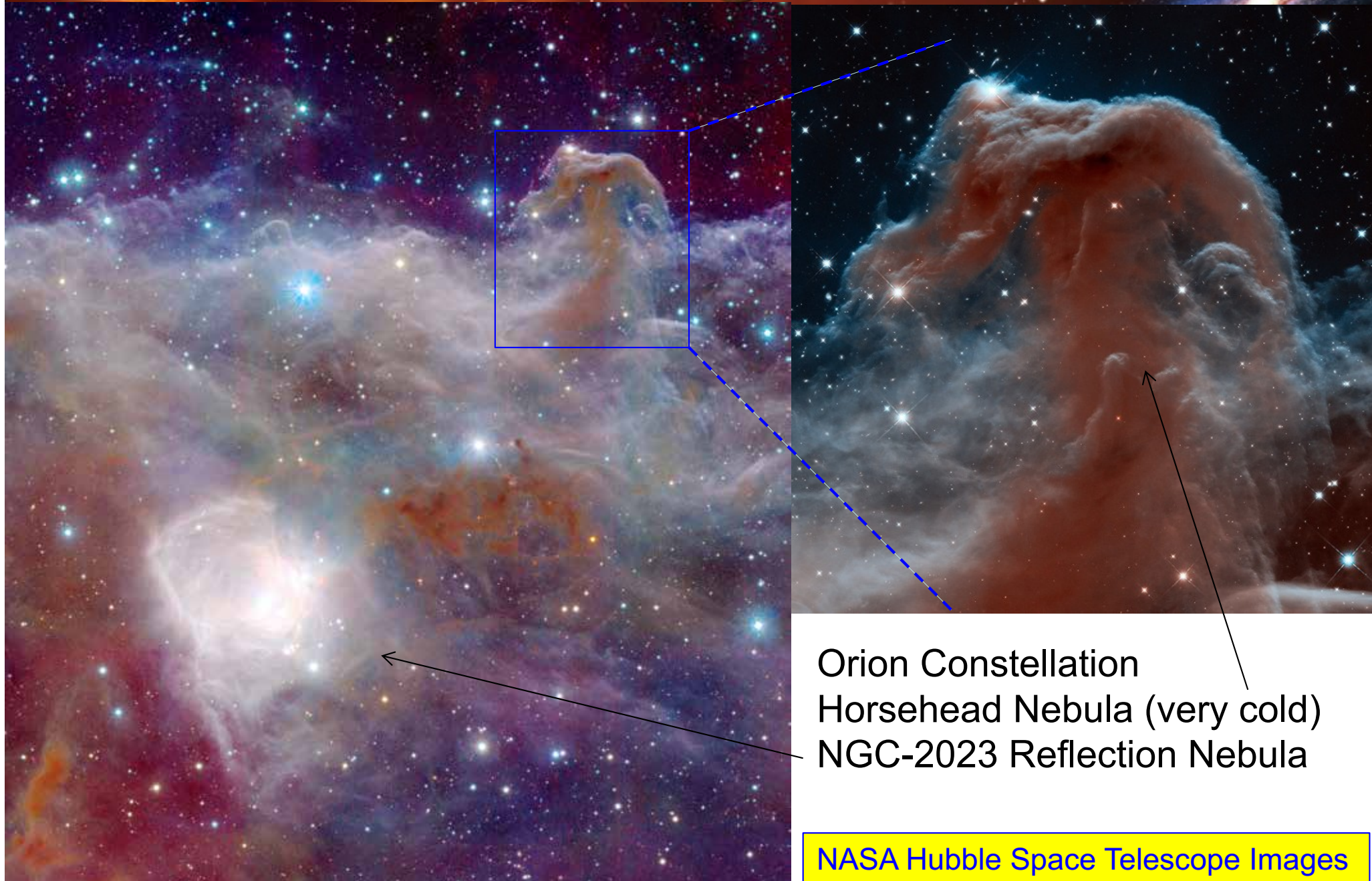


Similar Composition: Comets and Interstellar Ice Grains



Rosetta-Rosina observations found many more volatiles (O₂, N₂, S₂, Ar, etc.,) as well as non-volatiles such as glycine.

Interstellar Molecular Clouds: Birthplaces of New Stars





Rosetta Mission to Comet Churyumov-Gerasimenko (CG-67P)

Discovered by
Klim Ivanovich Churyumov
Svetlana Ivanovna Gerasimenko

Discovery site
Alma-Ata, Kazakh SSR, Soviet Union
Kiev, Ukrainian SSR, Soviet Union
Discovery date 20 September 1969

Aphelion 5.6829 AU (850,150,000 km)
Perihelion 1.2432 AU (185,980,000 km)

Eccentricity 0.64102
Orbital period 6.44 years

Dimensions
Large lobe: $4.1 \times 3.3 \times 1.8$ km
Small lobe: $2.6 \times 2.3 \times 1.8$ km
Volume 21.4 km^3 (5.1 cu mi)
Mass $(1.0 \pm 0.1) \times 10^{13} \text{ kg}$
Mean density 0.47 g/cm^3
Rotation period 12.4043 ± 0.0007 hours





Micro-Solvation of Ions Species in Cryogenic Water-Ice



Another 3 Years for the First Announcement

Gordon Research Conference 2003, Bates College, Lewiston, ME

WEDNESDAY

7:30 am - 8:30 am Breakfast

9:00 am - 12:30 pm **Reactive Species and Processes II**

Discussion Leader: **Zofia Mielke** (University of Wroclaw)

9:00 am - 9:40 am **Rui Fausto** (University of Coimbra)
"Matrix-Induced Changes of Low-Energy Conformational Levels Sequence: Proof for Molecules Showing Different Ground Conformational States in the Gas Phase and in Inert Gas Matrices"

9:40 am - 10:20 am **Bryce Williamson** (University of Canterbury)
"Jahn-Teller Coupling in the Ground and Excited States of the Ferricenium Radical Trapped in Ar"

10:20 am - 10:50 am BREAK

10:50 am - 11:10 am **Murthy Gudipati** (University of Maryland)
"Optical Spectroscopy of VUV Processed Cryogenic Water Ices: Astrophysical Relevance"

11:10 am - 11:50 am **Robert Sheridan** (University of Nevada)
"Cutting Corners-Organic Reactions at Very Low Temperatures"

11:50 am - 12:30 pm **Wolfgang Harbich** (Ecole Polytechnique Federale de Lausanne)
"Softlanding, Stability, and Optical Properties of Small, Size-selected Ag Clusters Embedded in Rare Gas Matrices"

12:30 pm Lunch

4:30 pm - 6:00 pm Poster Session

6:00 pm Dinner

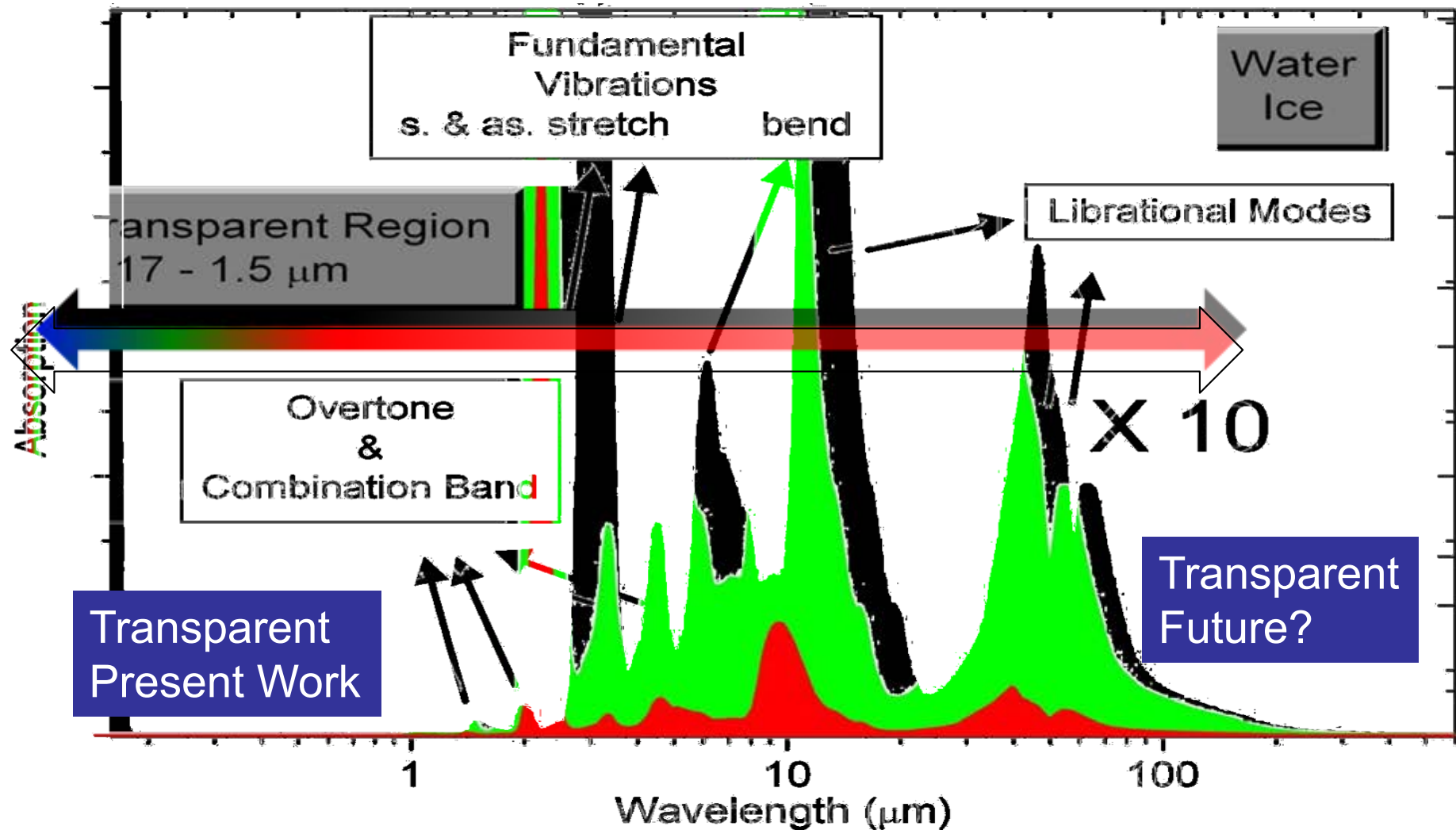
7:30 pm - 9:30 pm **Dynamical Processes in Matrices**



The Birth of UV-Spectroscopy of/in Water-Ice (2000)

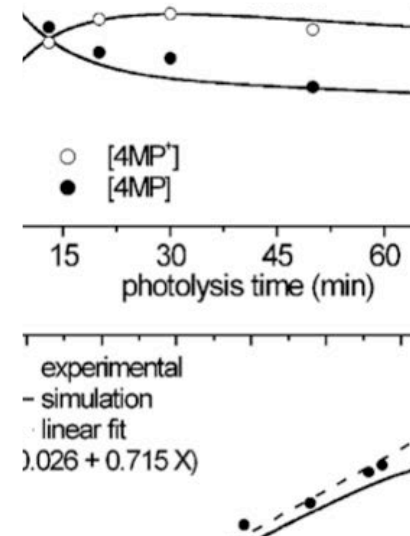
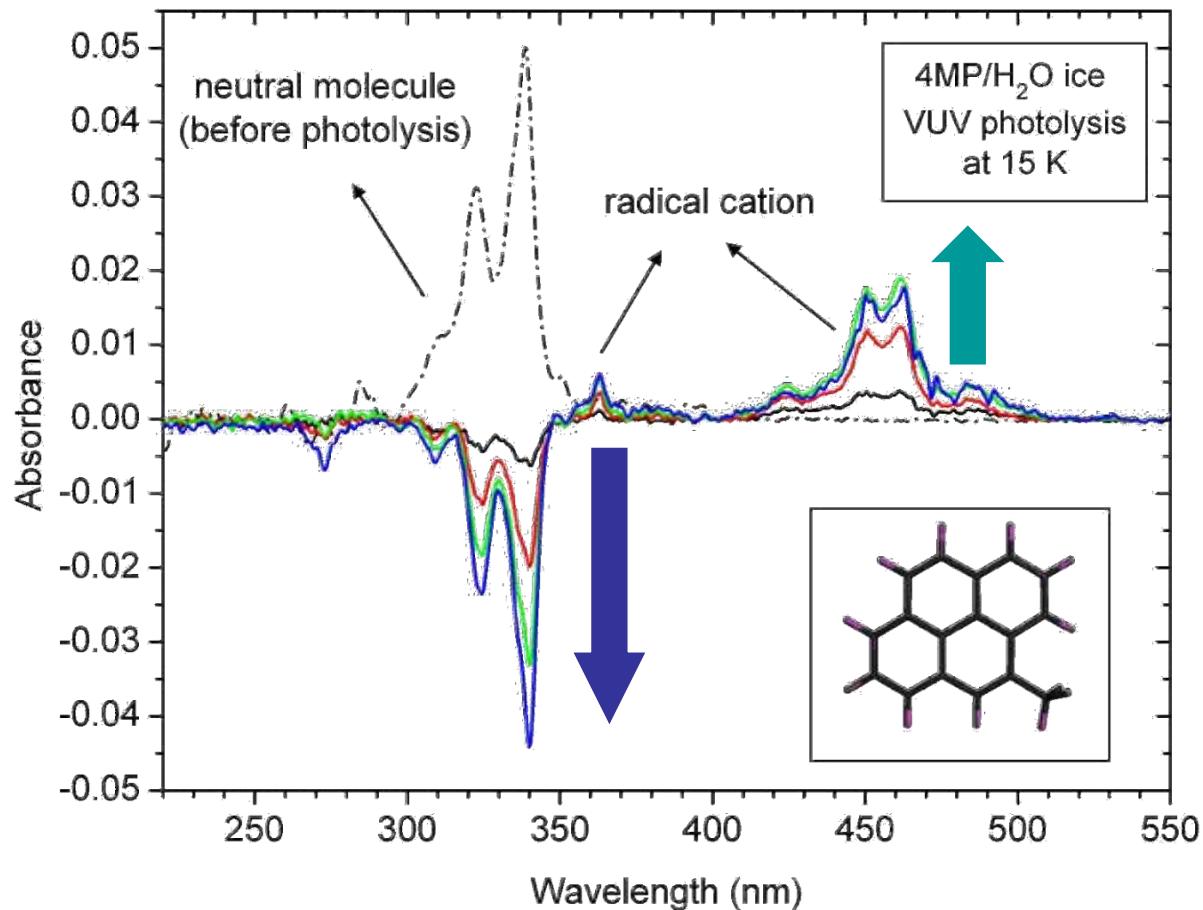
Necessity is the Mother of Invention: IR region is dominated by water – Optical the way to go

Electronic	Vibrations	Phonons	Rotations
UV	NIR MIR	FIR	THz Microwave





First Detection of Reactive Intermediates in Water-Ice Matrix

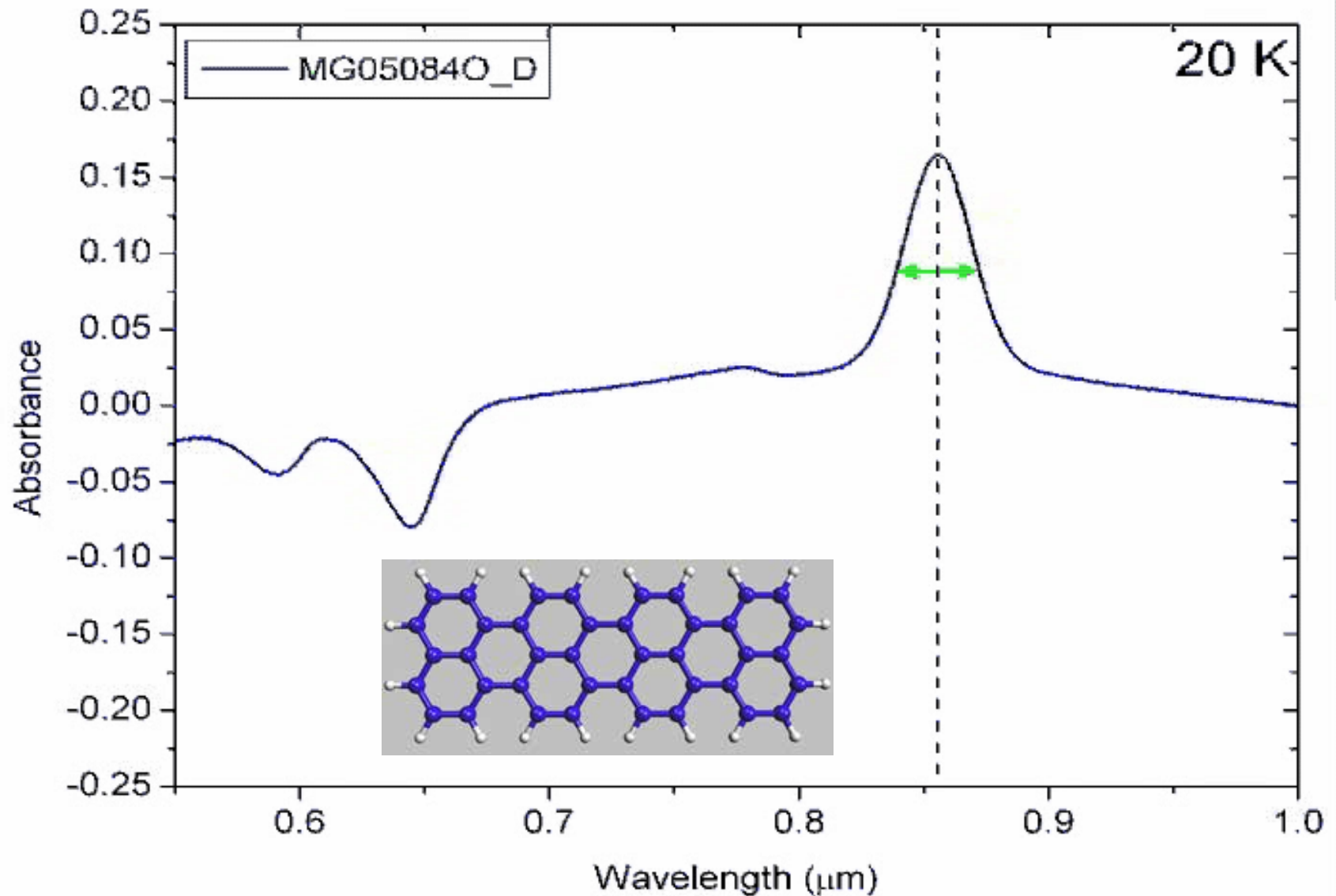


Gudipati & Allamandola, ApJ 596, L195 (2003)

First UV-VIS spectroscopy of PAHs in Ice
Positive Identification of PAH⁺ in Ice

NASA Unusual Stability of Large Ionized PAHs in Ice

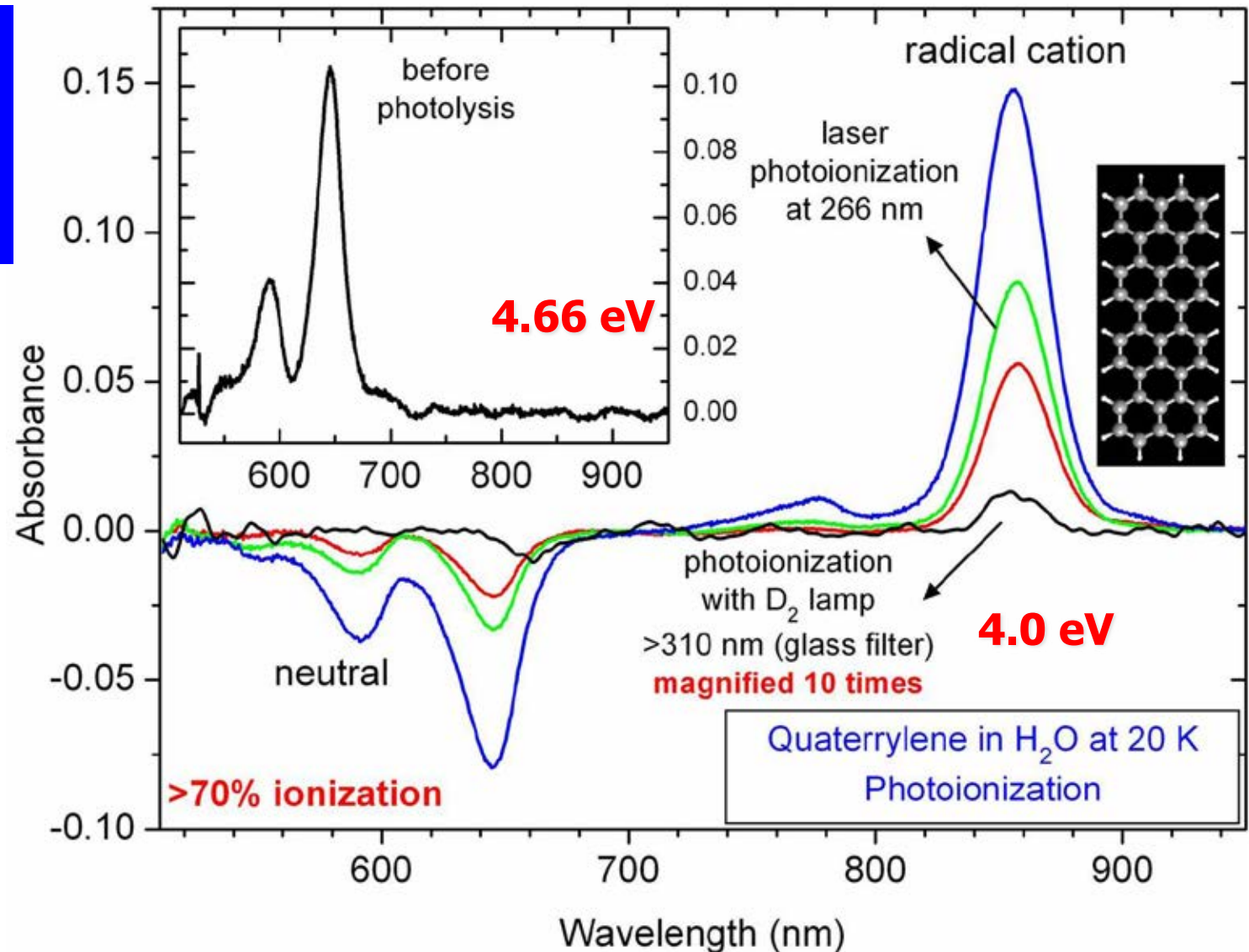
A One-Month Long Experiment at Ames amid Hiking in Sierras



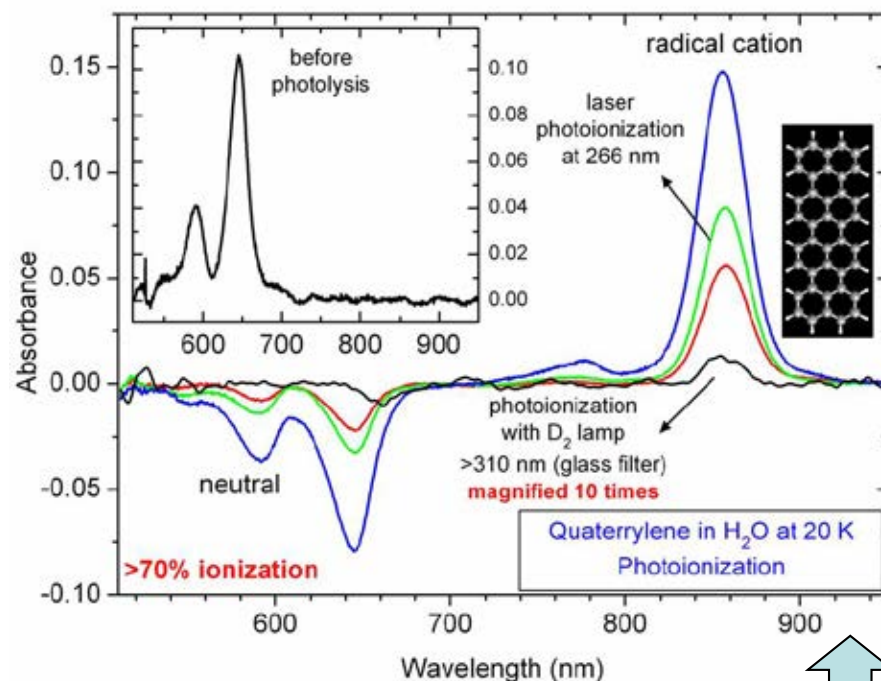
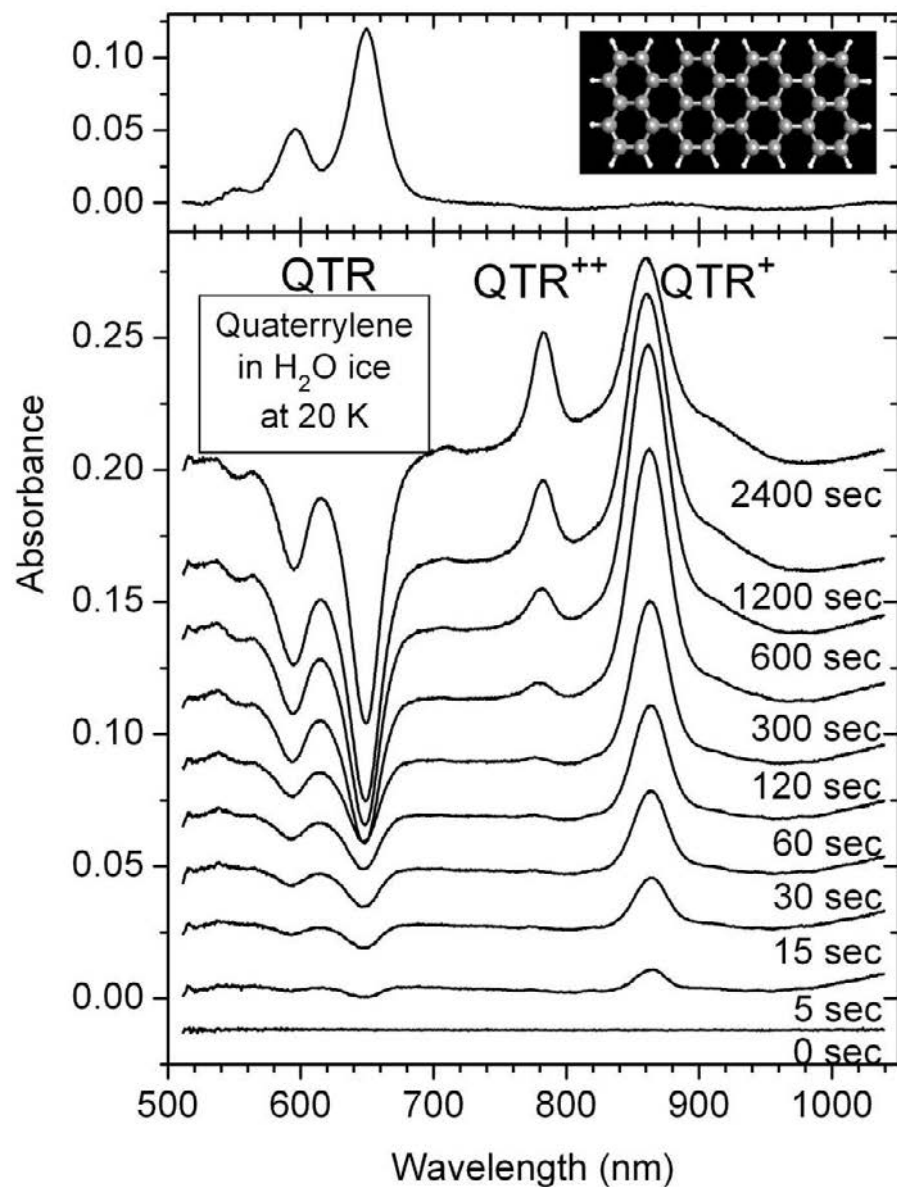


III. Lower Ionization Energies in Water Ices

I.E. (Gas-Phase)
6.11 eV (203 nm);
Ionization in H₂O
< 4 eV (> 310 nm)



NASA IV - Multiple Ionization of PAHs in Water-Ices

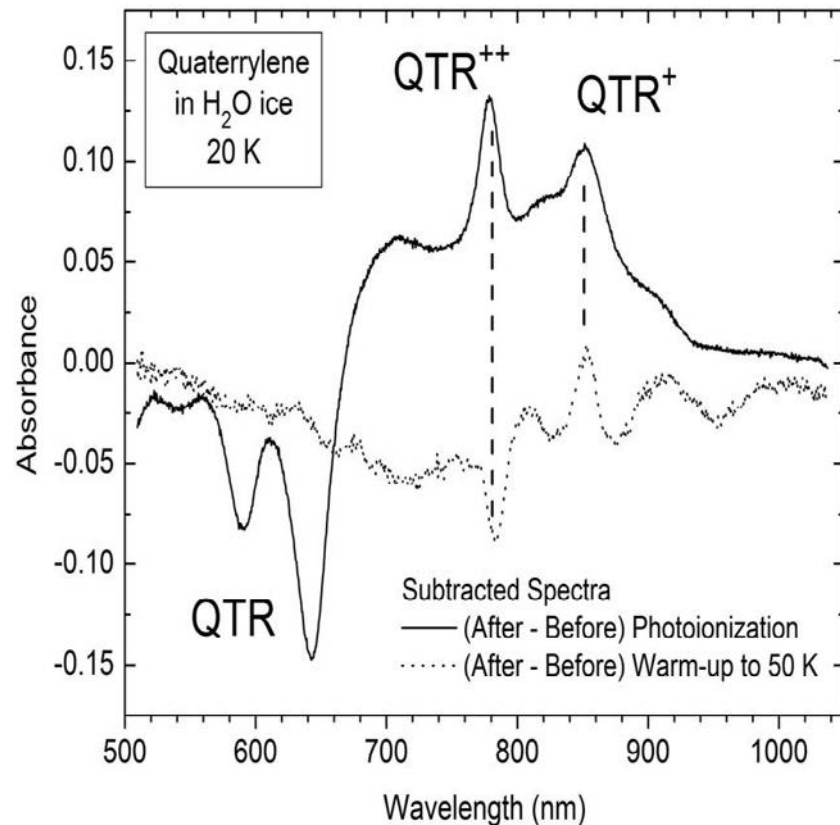


266 nm Laser
Ionization (4.66 eV)

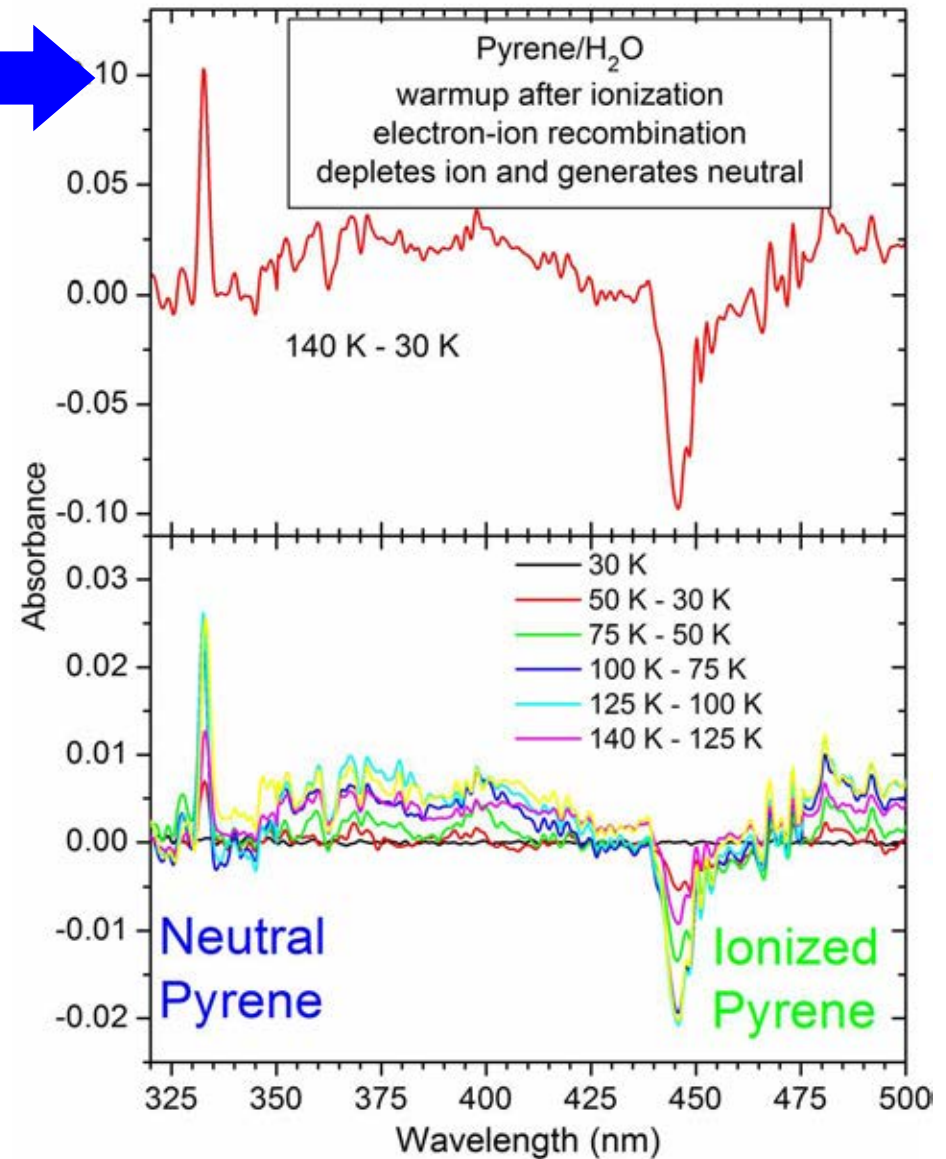
Plasma VUV
121.6 nm H Ly (α)
Ionization (10.2 eV)

NASA Storage of Charge (Ions & Electrons) in Ices

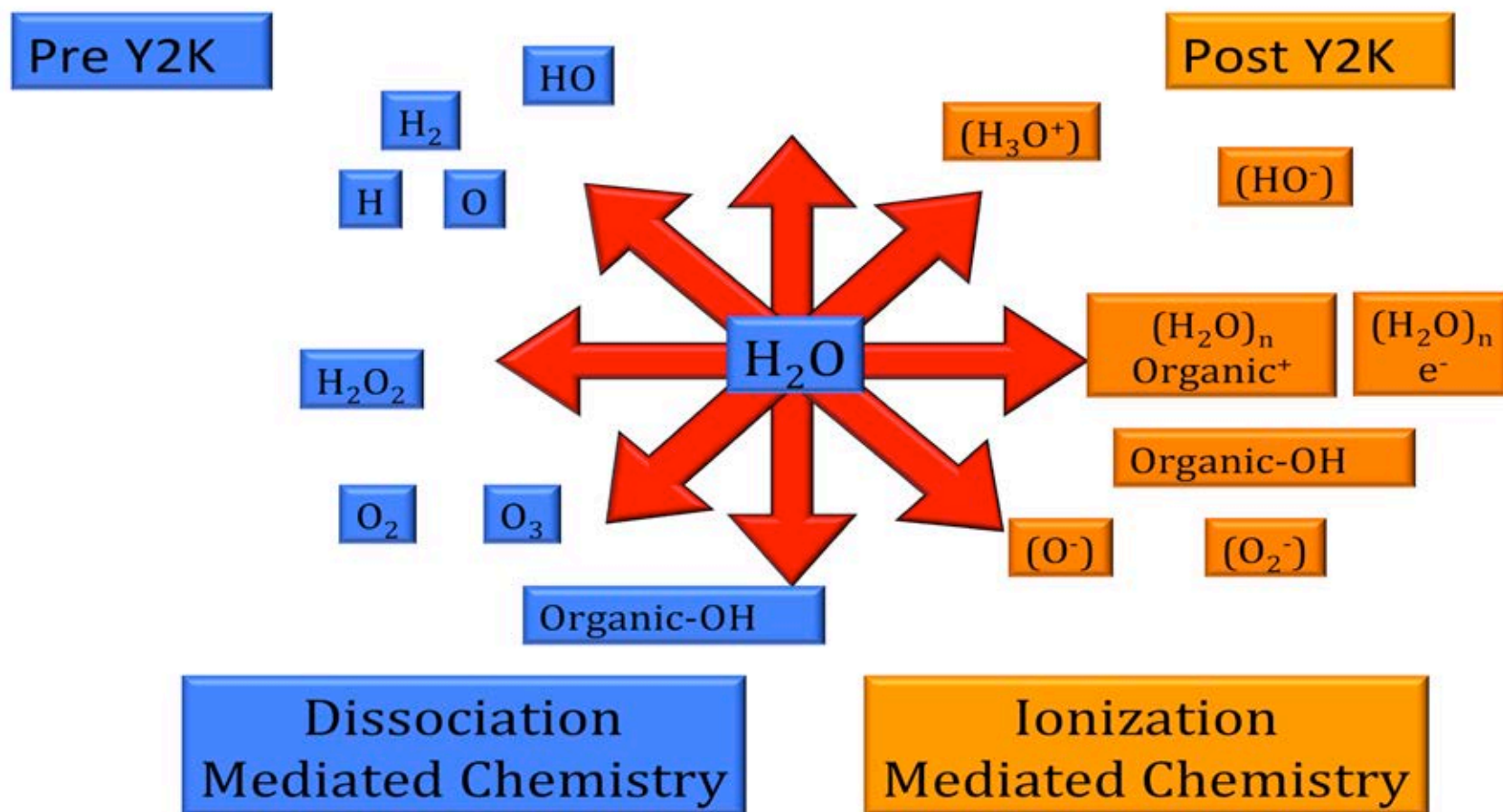
Thermal $\text{PYR}^+ + e^- \rightarrow \text{PYR}$
recombination in ices



Thermal $\text{QTR}^{++} + e^- \rightarrow \text{QTR}^+$
recombination in ices



Ionization: Key Step in Radiation Processing of Organics in Water/Ice



Murthy S. Gudipati and Paul D. Cooper,
 Chemistry in Water Ices: From Fundamentals to Planetary Applications
 in *"The Science of Solar System Ices"*,
 M.S. Gudipati and J. Castillo-Rogez (eds.), Springer, NY, 2013.



Water-Ice UV Spectroscopy - Started in 2001



NASA Ames – Truckee Cross-Country Skiing



By the time ICLTC 2008 (Helsinki) Matrix-Isolation in Water-Ice became Mainstream





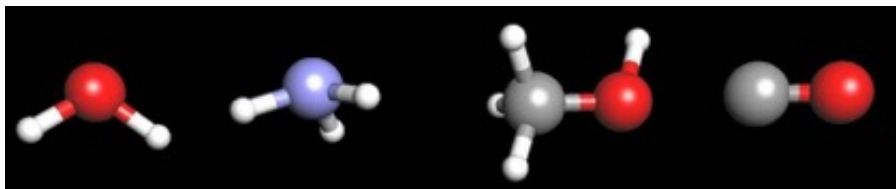
Complex Organics

Complex Organics – How and Where From?



Refractory/Complex Organics: Where and How they are formed?

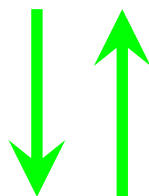
Cryogenic
Cosmic Ices



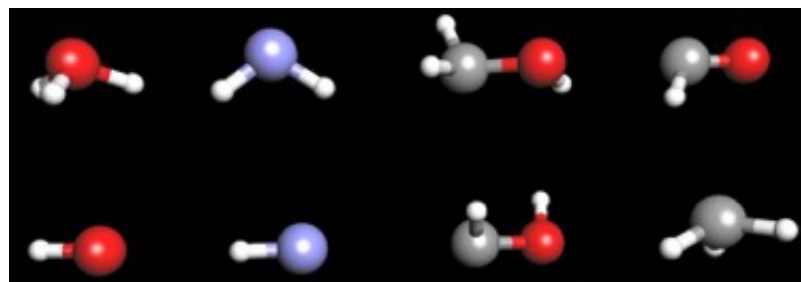
Raw Material
 H_2O , NH_3 , CH_3OH , CO

Photons/Electrons
Cosmic Rays
Debris/Collisions

Temperature



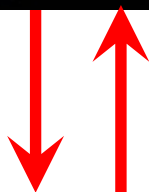
Radicals,
Ions,
Electrons, &
Molecules



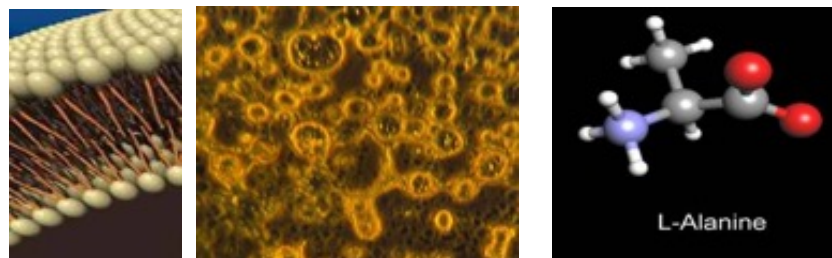
Building Blocks
Atoms, Radicals & Ions

Temperature

Photons/Electrons
Cosmic Rays
Debris/Collisions



Amino Acids,
Micelles, etc.

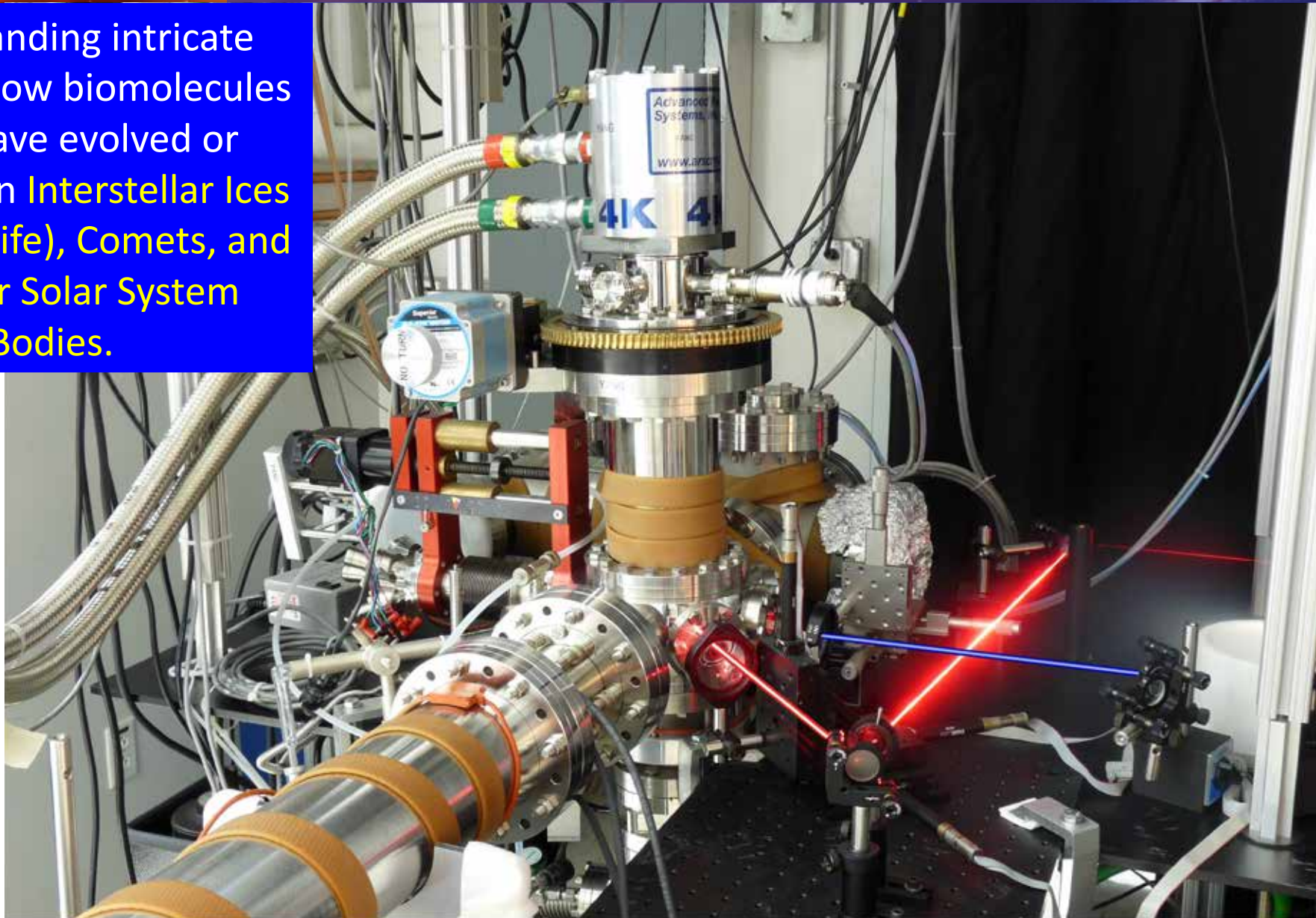


Biomolecules
Amino Acids etc.

Understanding Prebiotic Chemistry in Comets

At Murthy's Ice Spectroscopy Lab (ISL) @ JPL

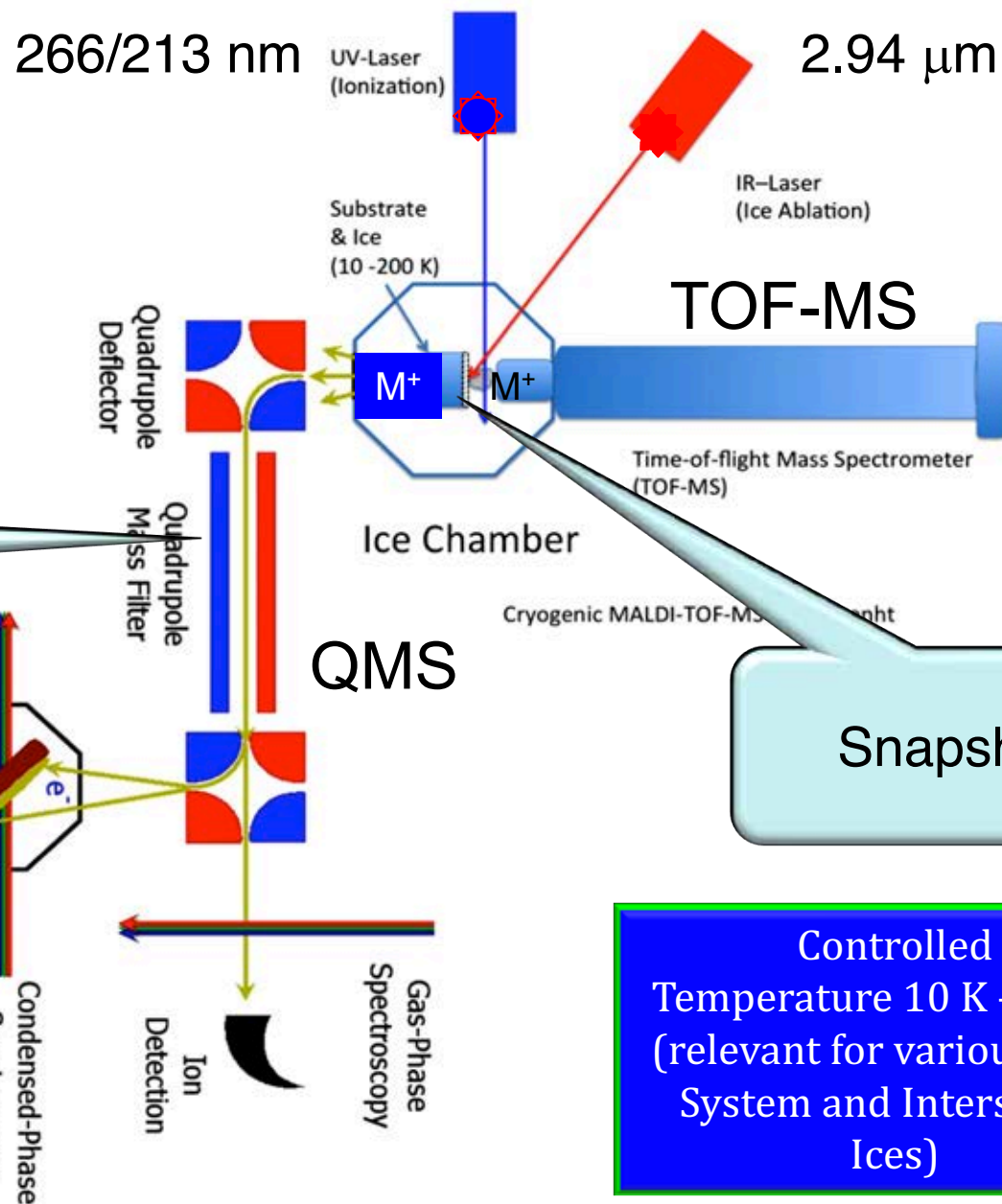
Understanding intricate details of how biomolecules could have evolved or degraded in **Interstellar Ices (Origin of Life), Comets, and on other Solar System Bodies.**



NASA

Snapshots of Chemical Reactions: 2S-LAI-TOFMS

Identification of atoms and molecules produced at various ice temperatures and radiation does
Interstellar & cometary ice chemistry
Evolution of prebiotic molecules



Mass Selection

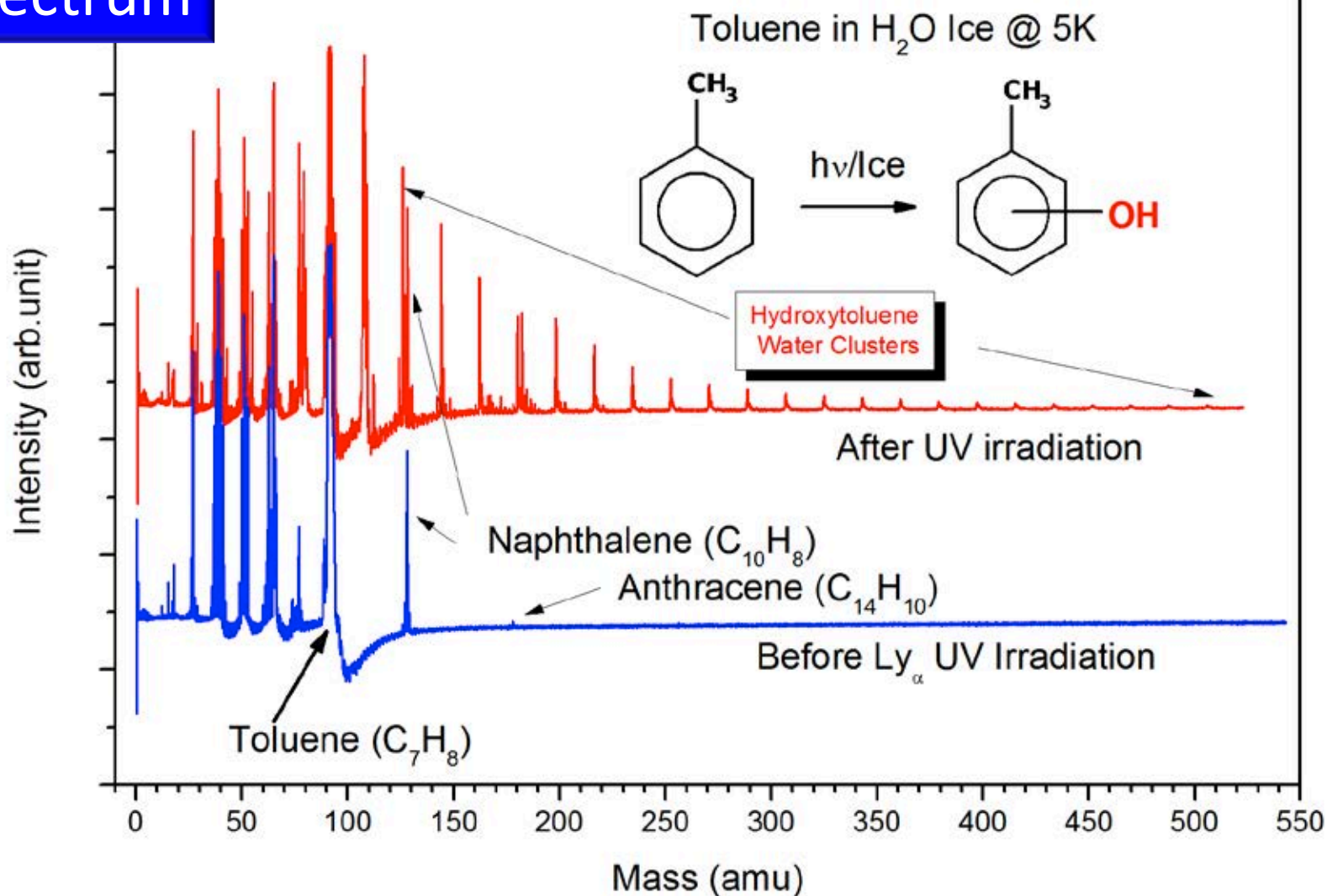
Isolation
&
Analysis

Snapshot

Controlled
Temperature 10 K – 200 K
(relevant for various Solar
System and Interstellar
Ices)

NASA Oxygenation of Organics in Ices under Radiation

2S-LAIMS Spectrum

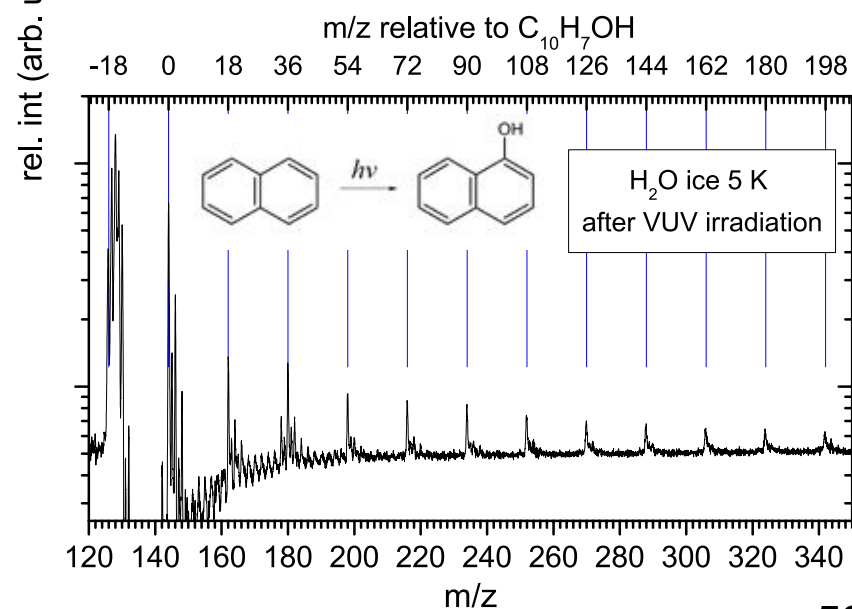
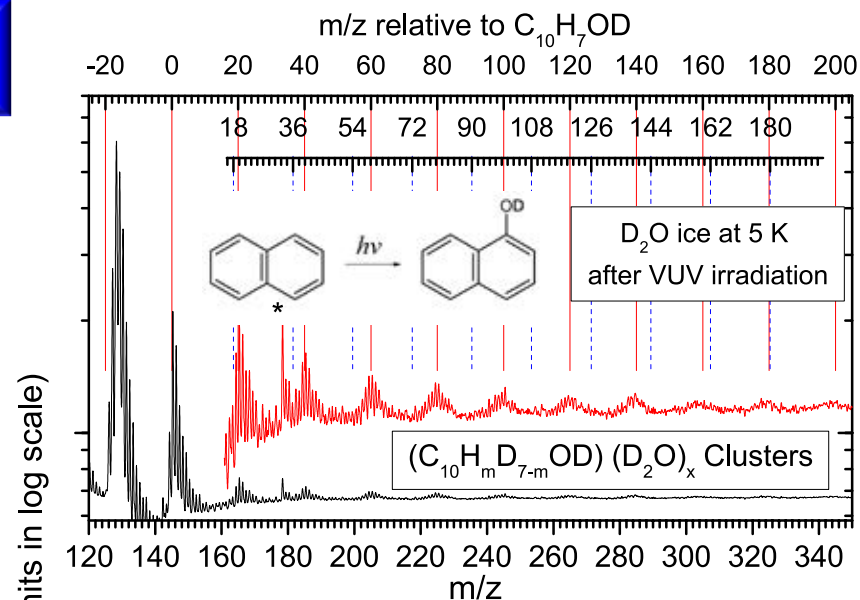
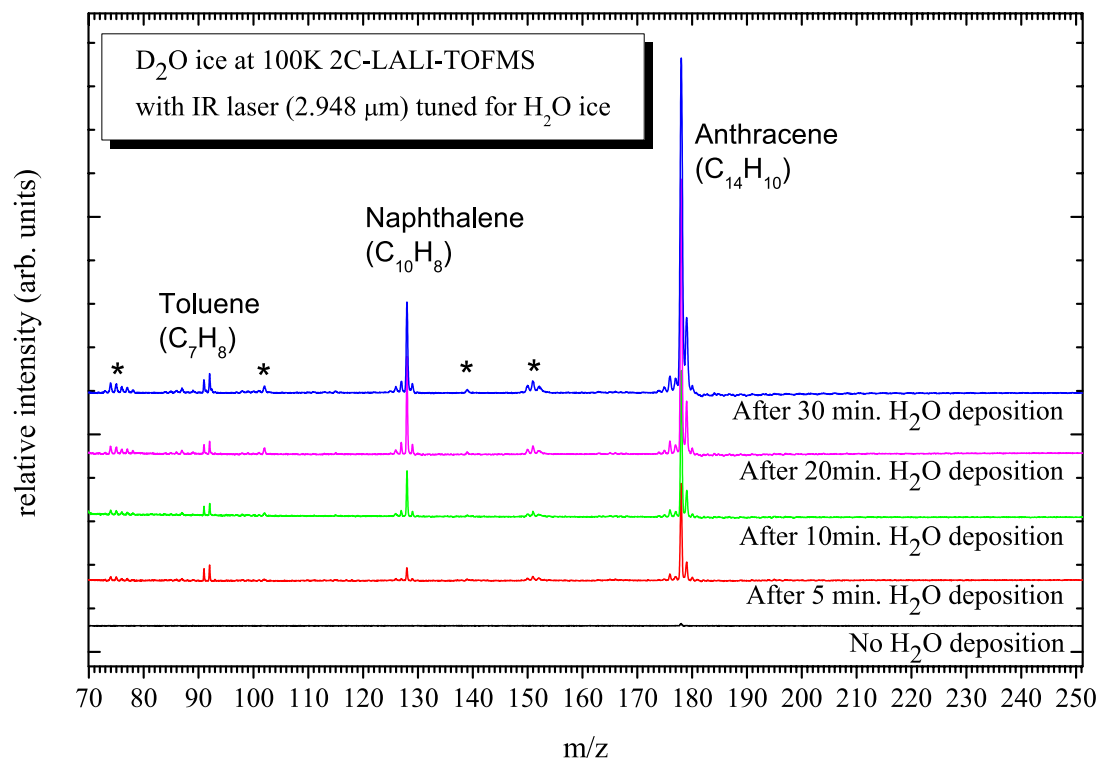


Gudipati & Yang ApJL 756, L24, 2012

Even under coldest interstellar conditions

Demonstration that IR Ablation Laser Does NOT cause Chemistry

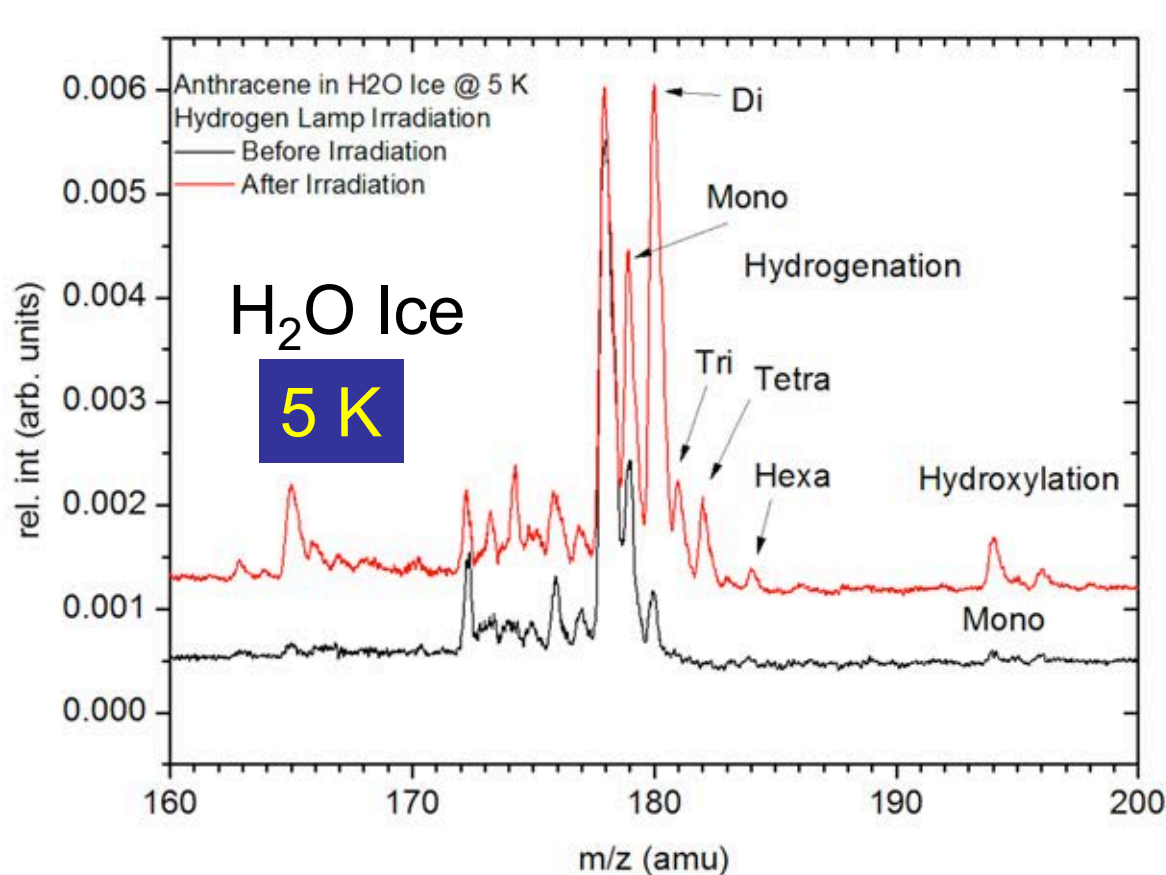
2S-LAIMS TOF-Mass Spectrum



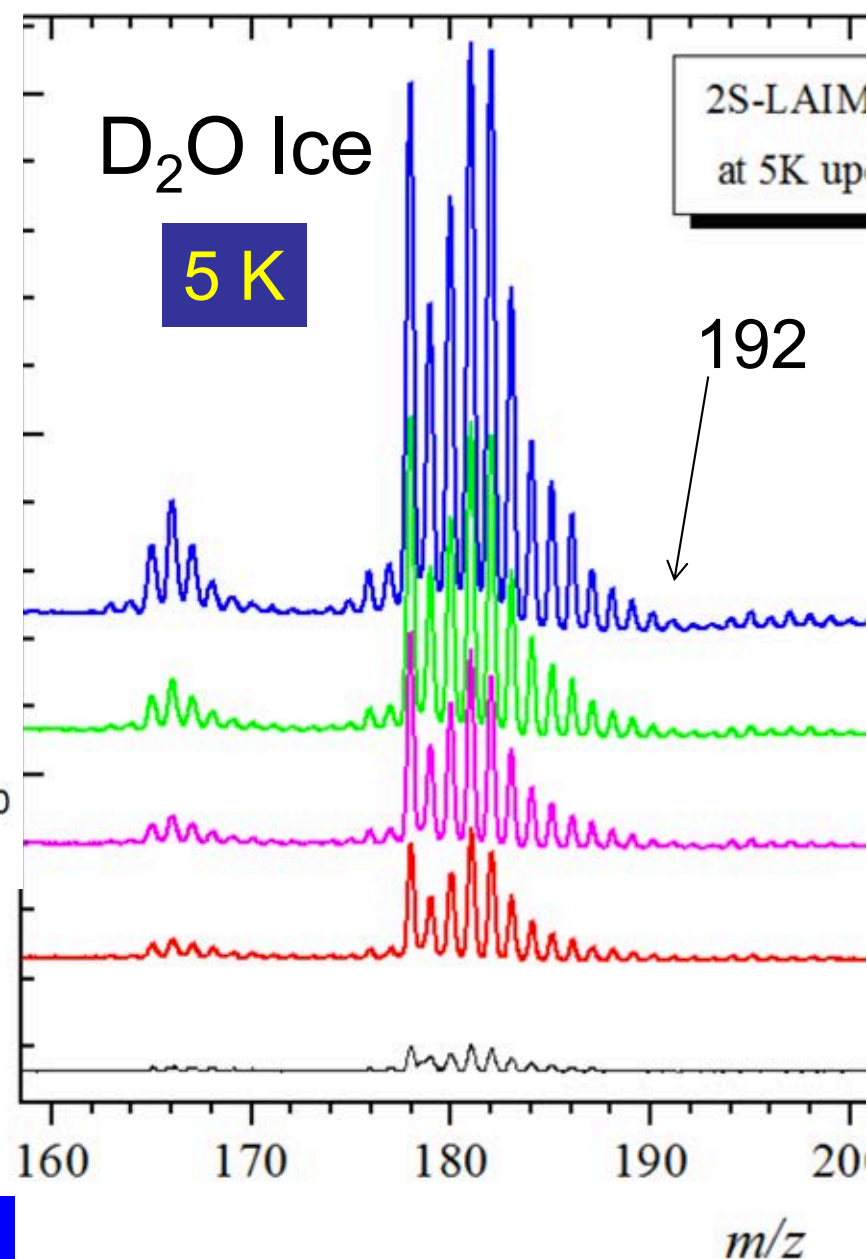


Deuteration and Photo H/D Exchange

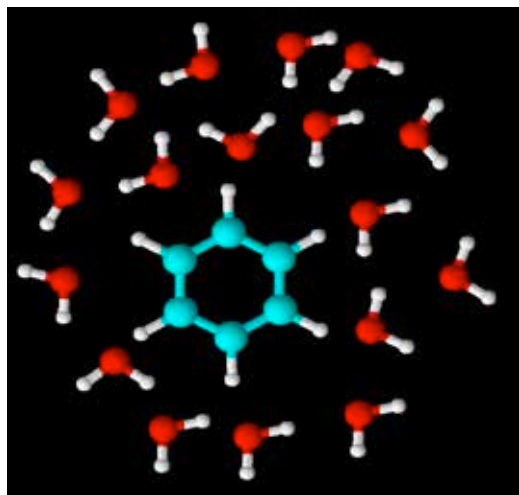
2S-LAIMS TOF-Mass Spectrum of Anthracene ($C_{14}H_{10}$) 178amu



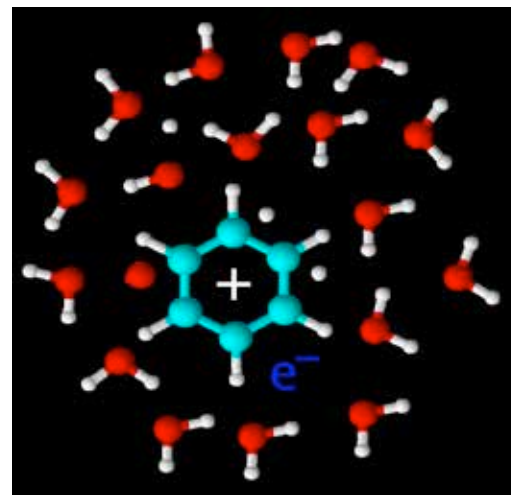
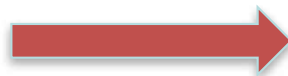
Caution to be exercised
When interpreting D/H ratios



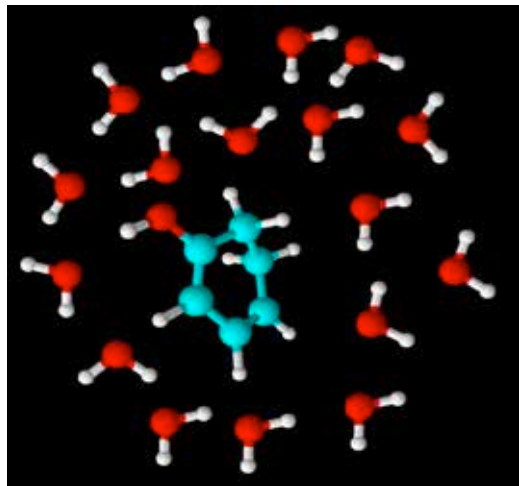
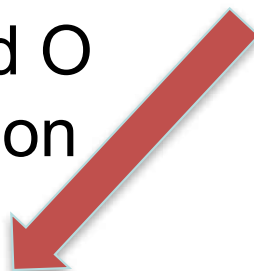
Ionization-Mediated Radiation-Chemistry in Ices



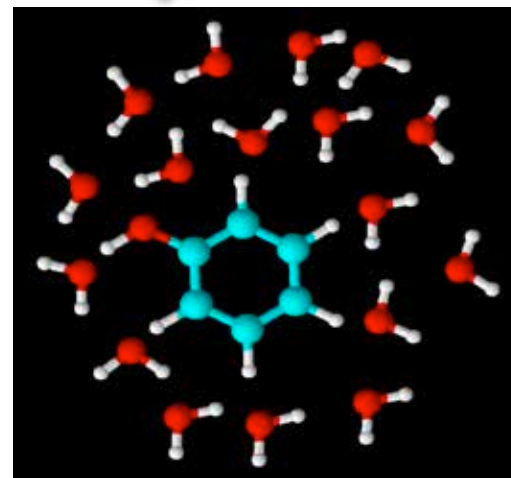
Radiation



H and O
addition



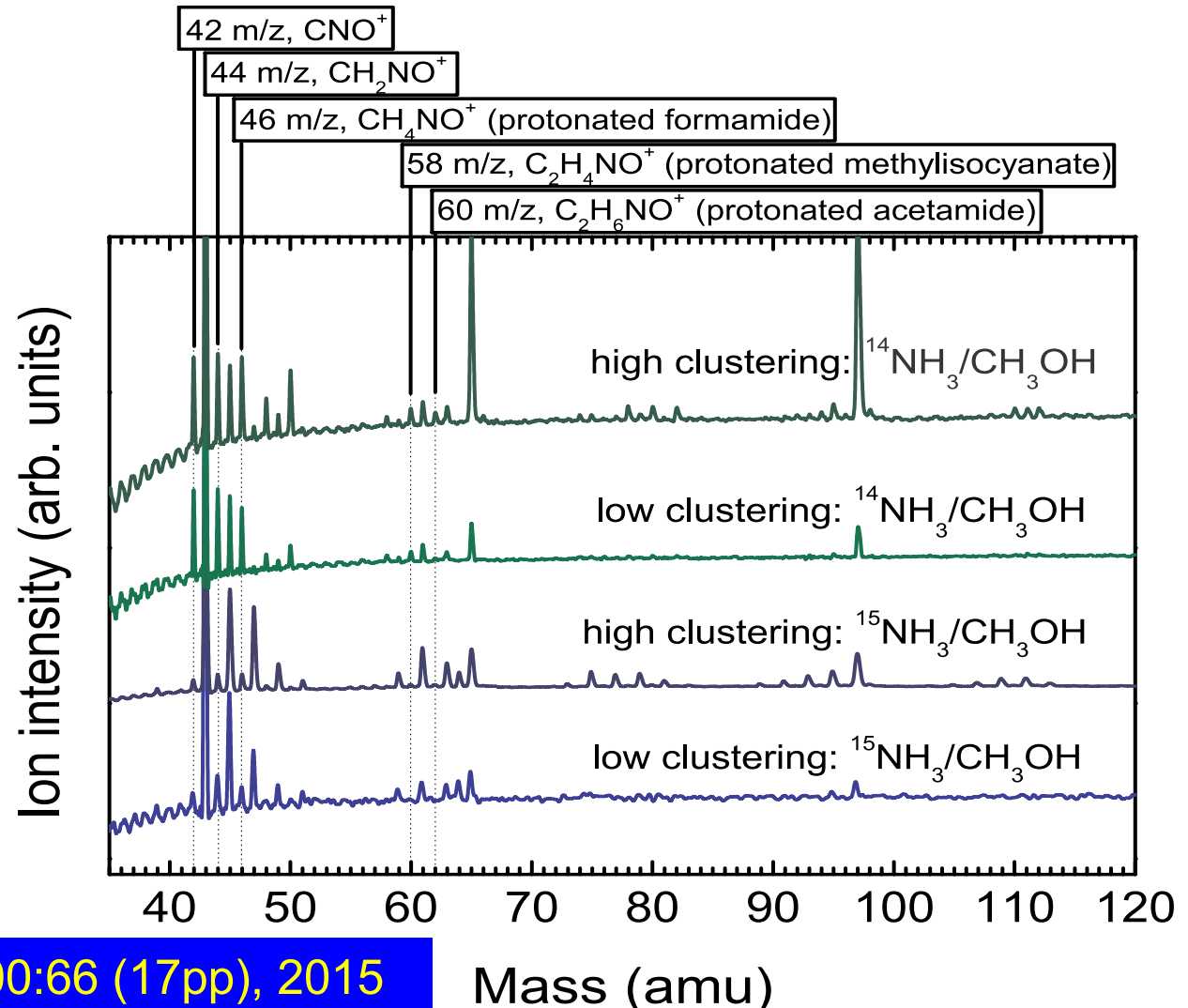
O-atom
addition



5 K

Snapshots/Scooping the Evolution of Astrophysical Ice Analogs

Interstellar /
Cometary Ice
Analogues
Produce Key
Building Blocks
Of Life upon
Radiation
Processing

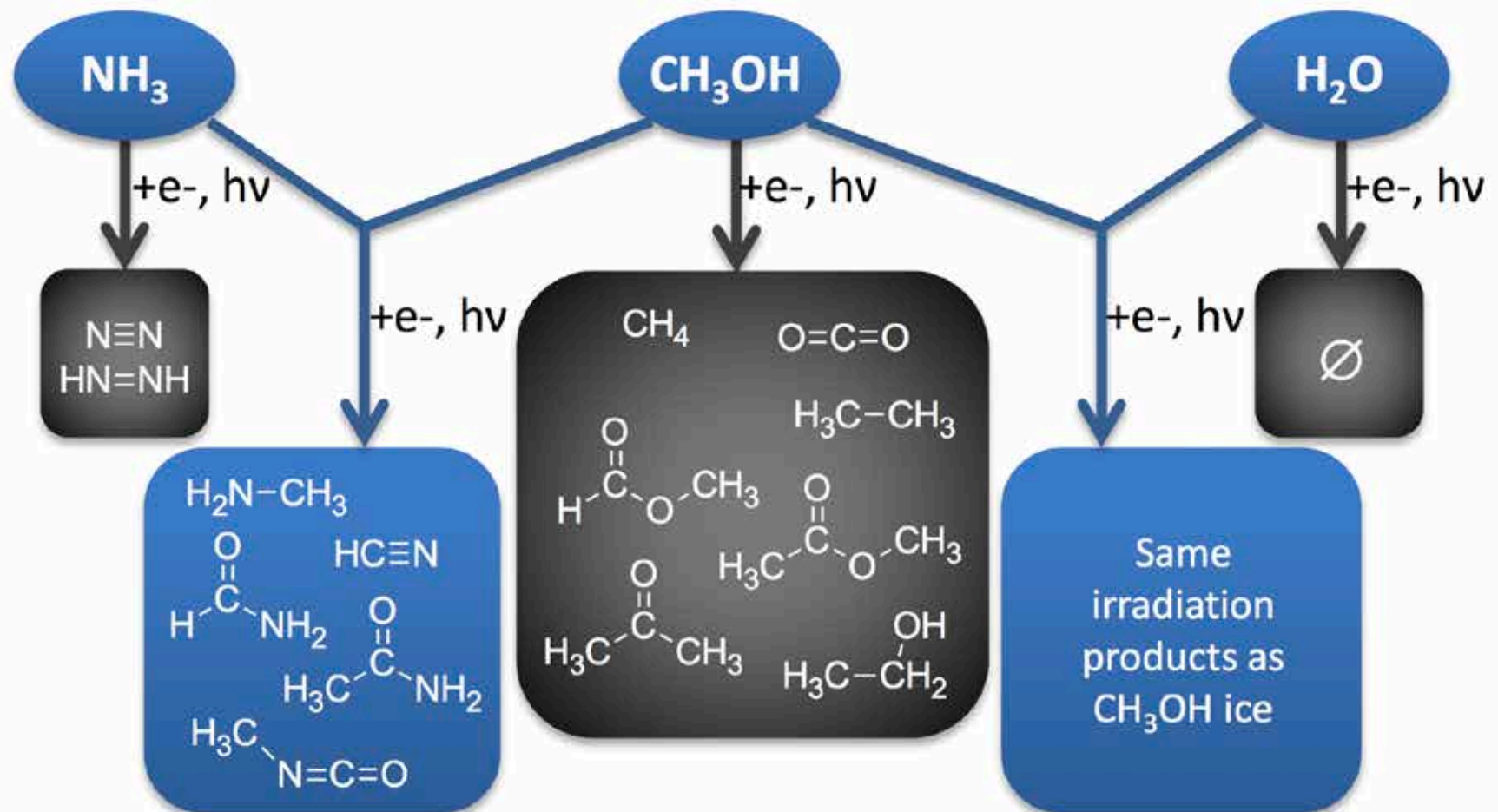


Henderson and Gudipati ApJ - 800:66 (17pp), 2015



Molecules found in interstellar ice analogs

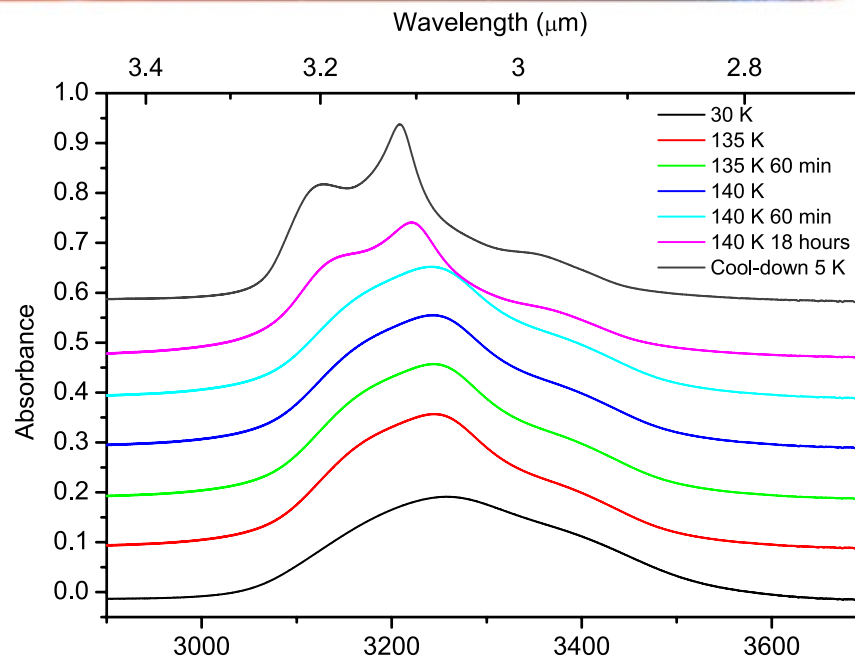
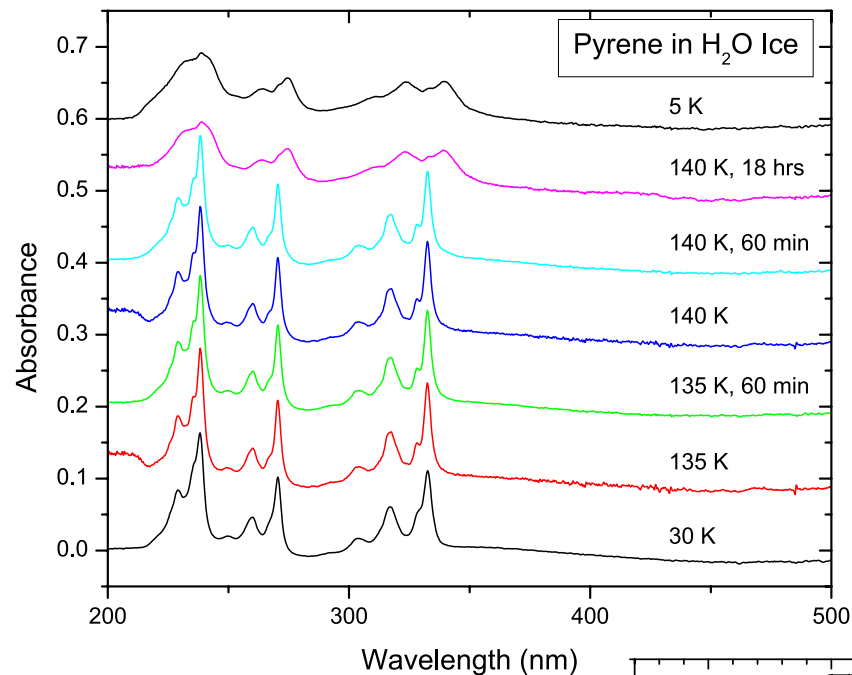
Irradiation Products of Single and Dual-Component Ices, 5 K



Many of these molecules are detected by Rosetta-ROSINA

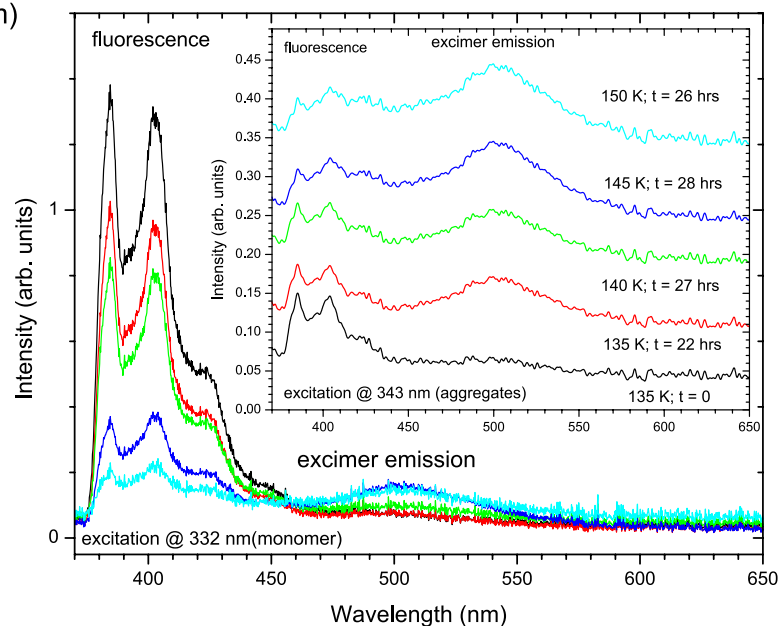
NH₃ less reactive than CH₃OH under radiation

Simultaneous UV & IR Absorption + Fluorescence Pyrene in H₂O Ice



UV - PAH

Flu - PAH



Wavenumbers (cm^{-1})

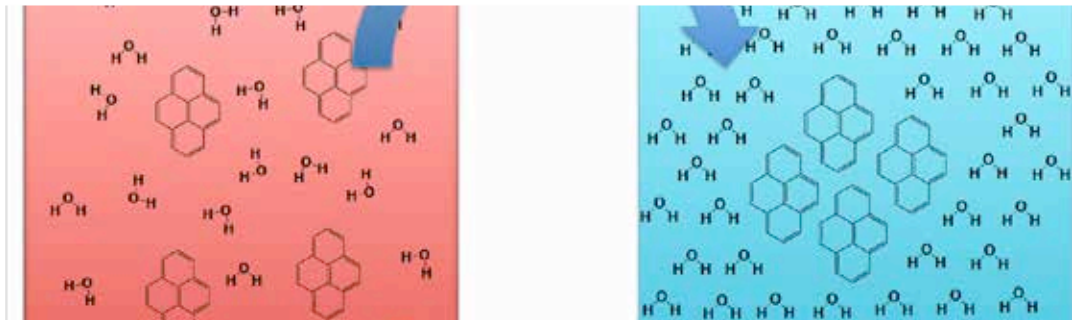
IR - Ice

Lignell & Gudipati
 J. Phys. Chem A.
 119 (2015) 2607

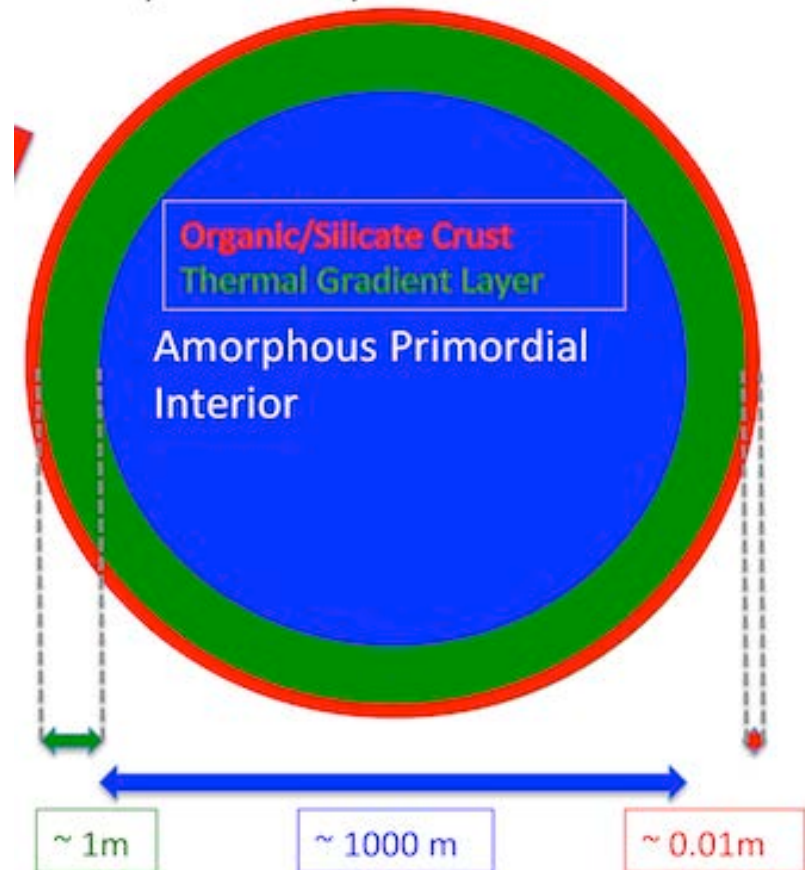


Are Comets Like Deep Fried Ice Cream?

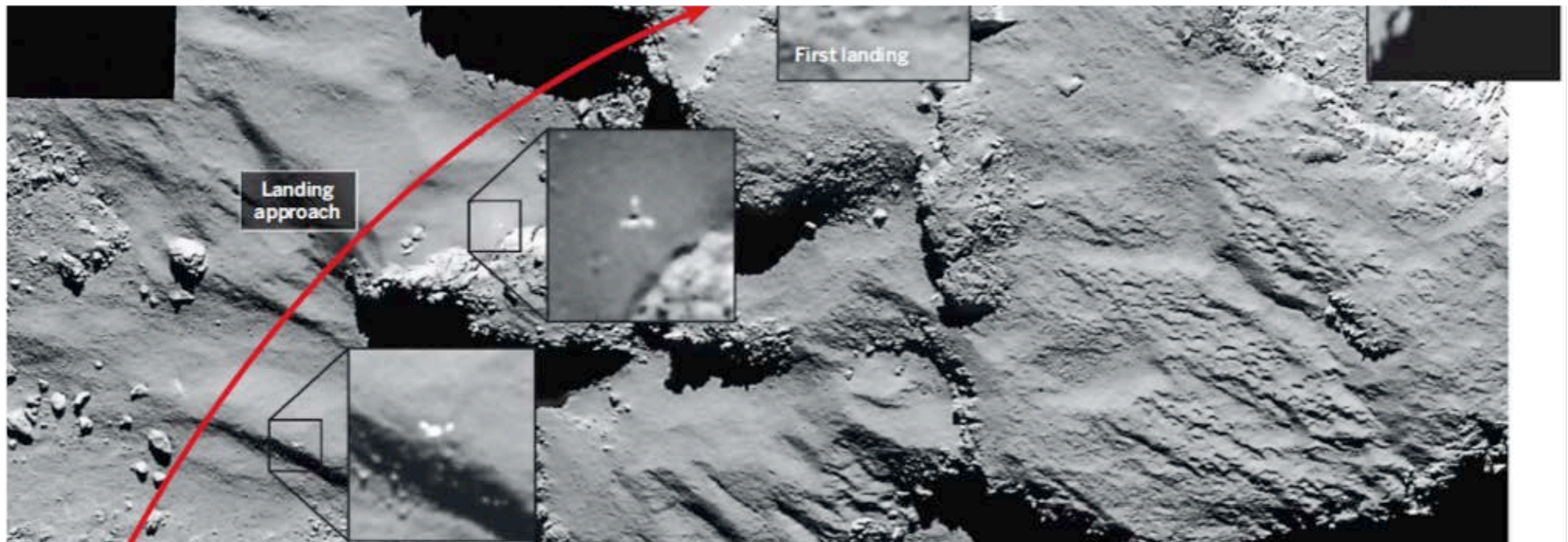
Rosetta (ESA/NASA) found ~10 cm Crust



Crust ~ 1cm
Processed ice ~ 1m
Unprocessed primordial ice >1m

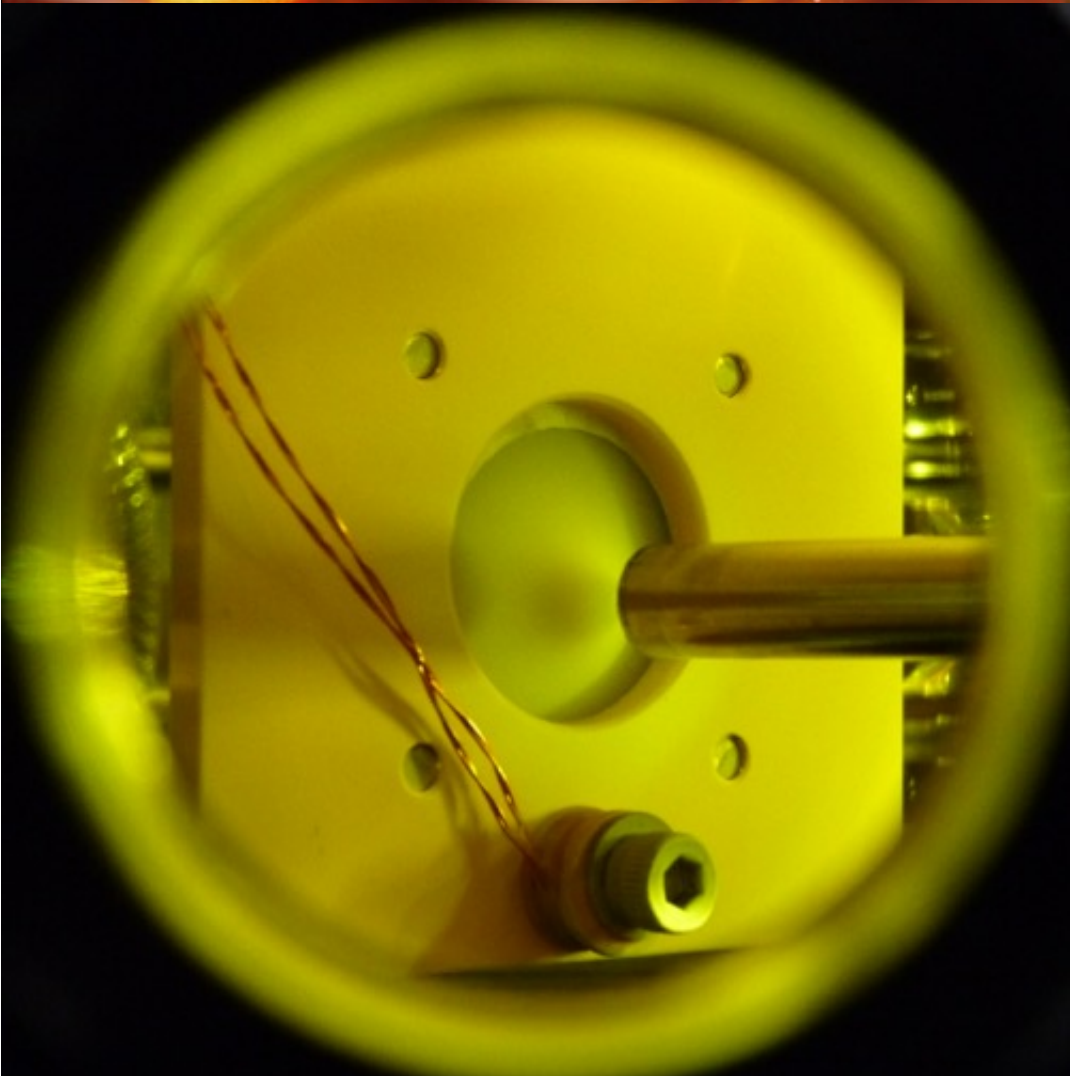


Lignell & Gudipati
J. Phys. Chem A.
119 (2015) 2607

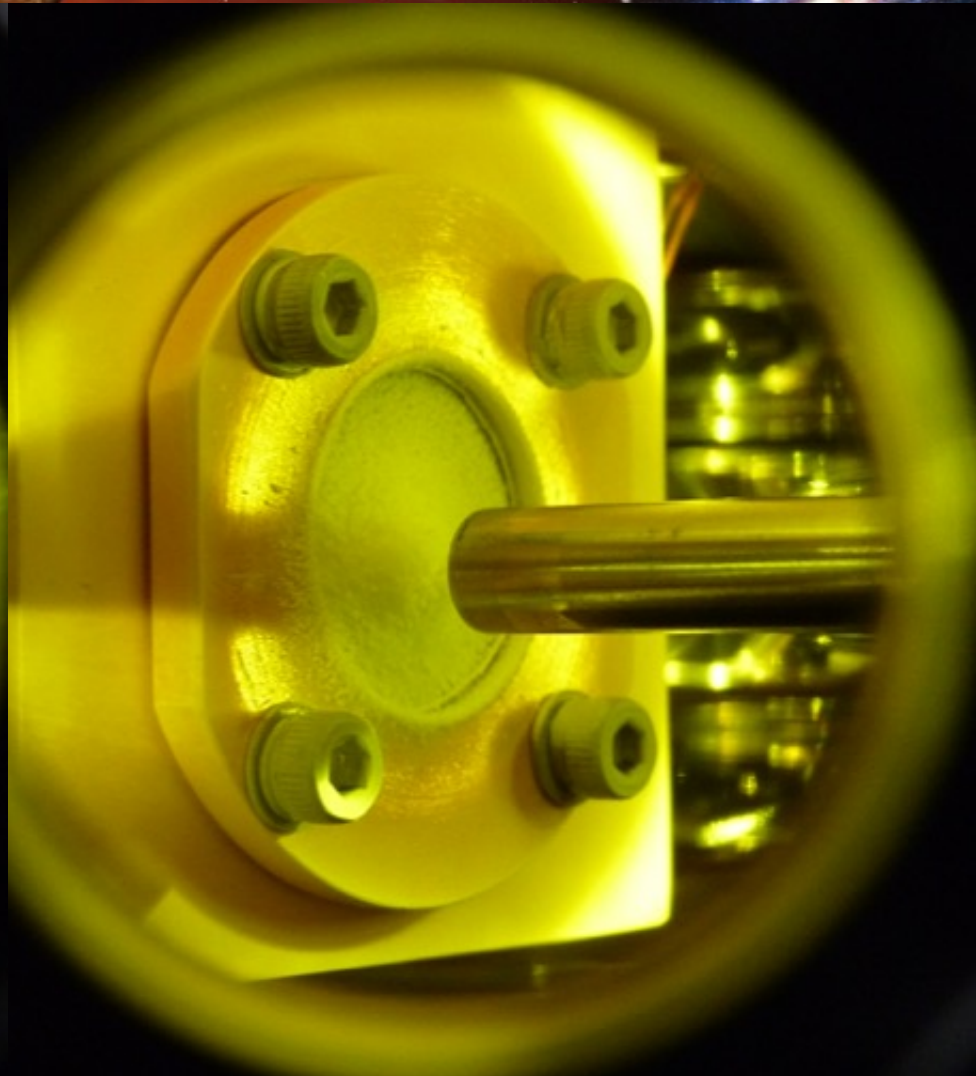




Macroscopic Amorphous Ices in the Lab: Simulating Interstellar & Comet Ices



150 K Deposition
(Crystalline)



5 K Deposition
(Amorphous)



Complex Organics

**Complex Organics:
Already formed in Molecular Clouds**



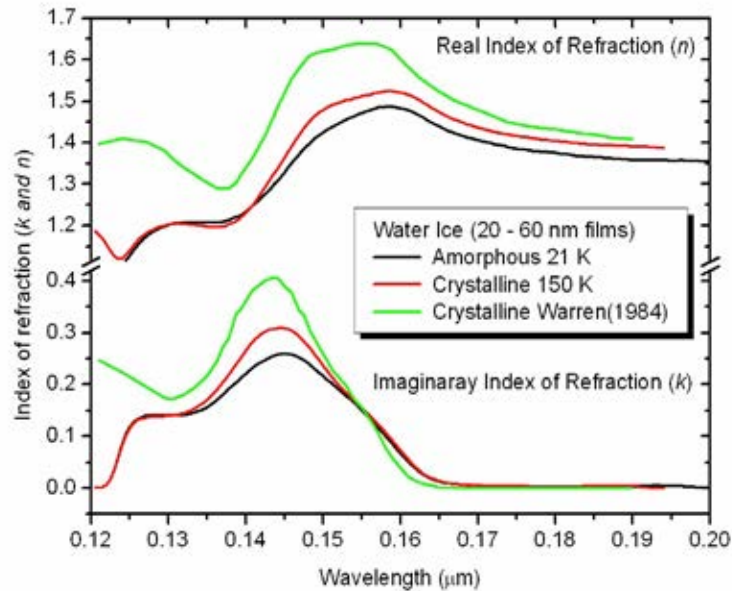
H₂O Ice & Super Volatiles

How are Super Volatiles Trapped in H₂O Ice?

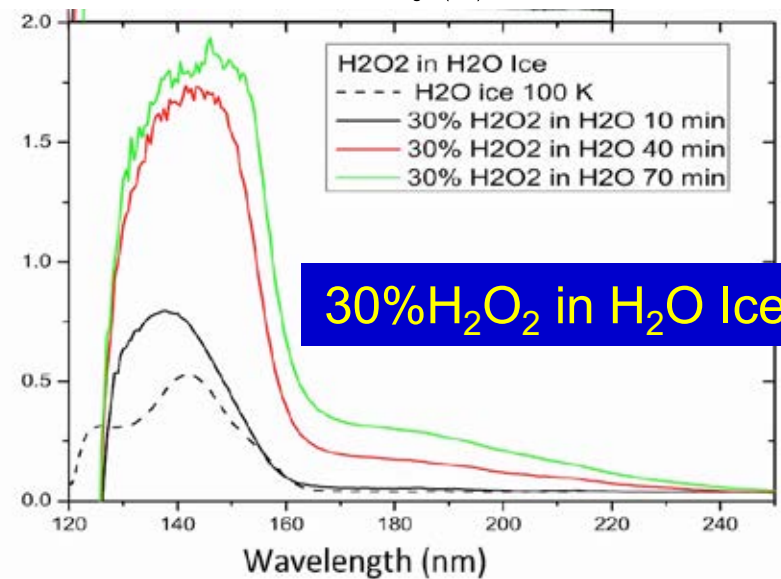
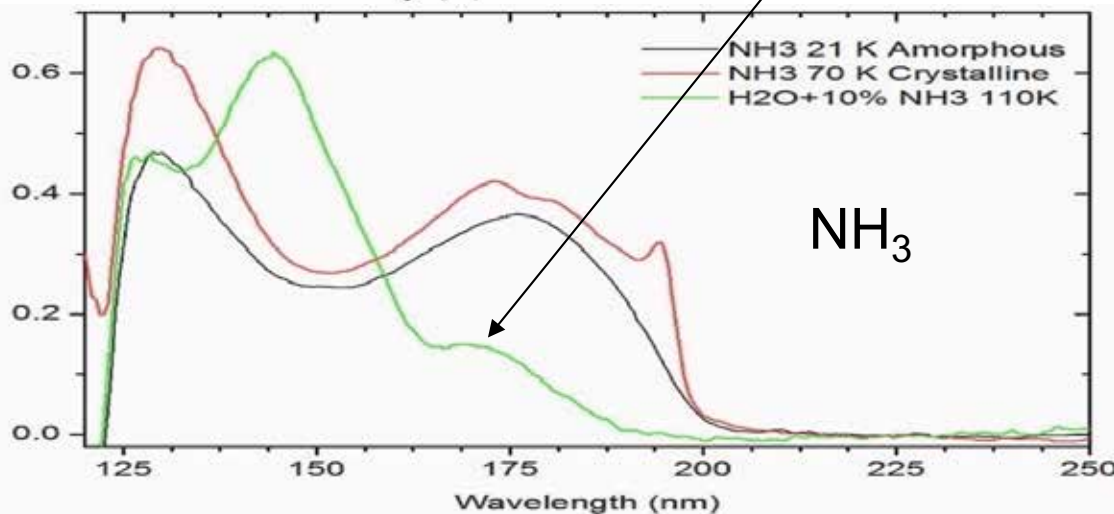
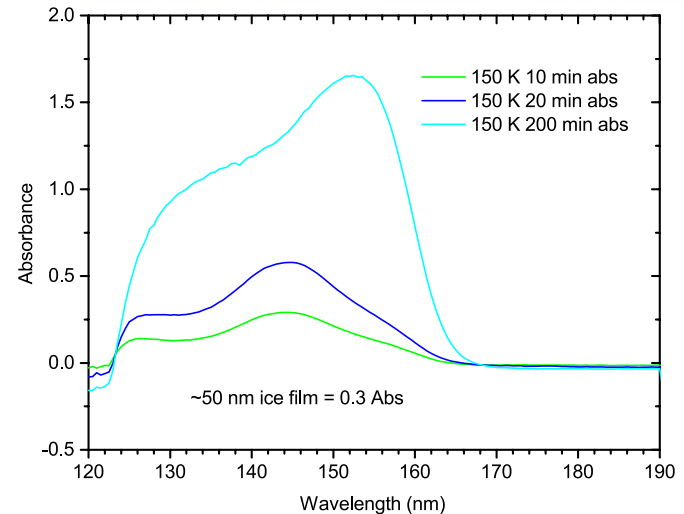


Ice Composition VUV Studies

Absorbance of H₂O Ice



Strongly Bonded

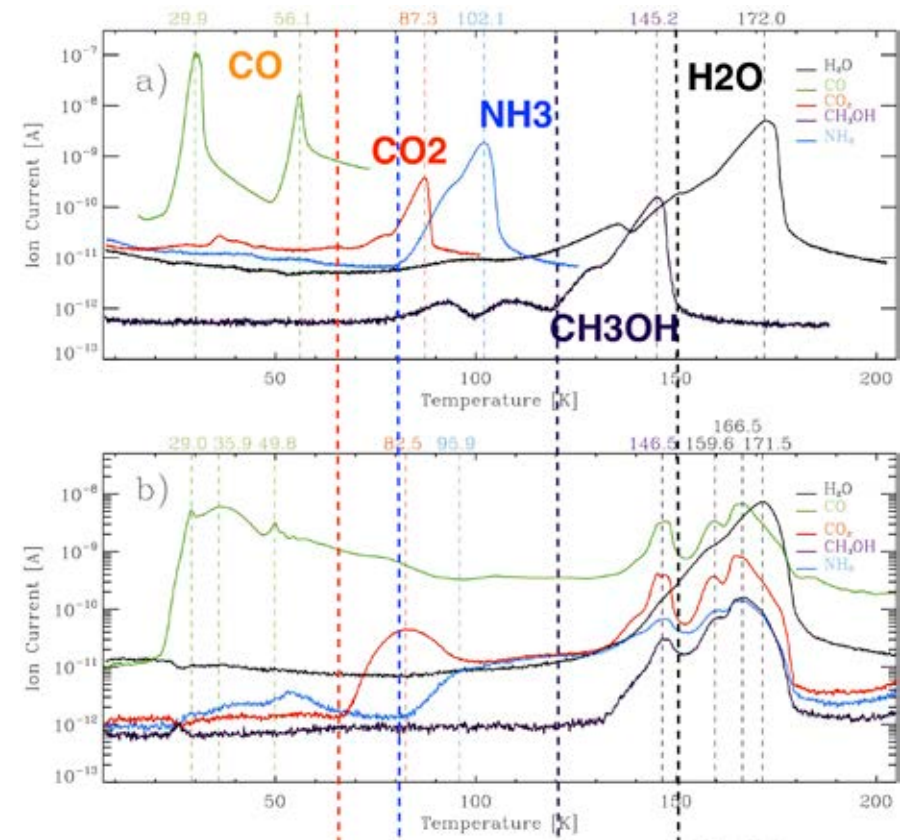
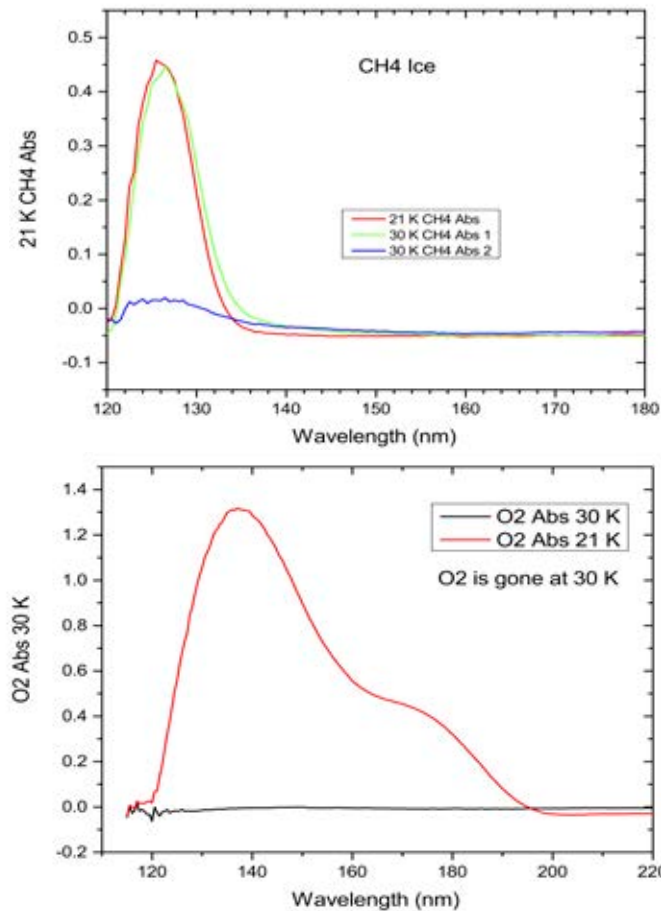


Top: VUV Optical Constants of Pure H₂O Ice
Bottom: Absorption Spectra of NH₃ and H₂O ice with 10% NH₃



Depletion Temperatures of Volatiles

Crystalline H₂O Ice <160 K; Amorphous H₂O Ice <<80 K
CO₂ Ice <70 K; Super Volatiles ~30 K



Gudipati et al., (NIST, VUV) – to be published

Martin-Domenech et al., A & A 2014, 564



Amorphous vs. Crystalline H₂O Ice

A Comet's Nucleus – What is it?
Amorphous or Crystalline?

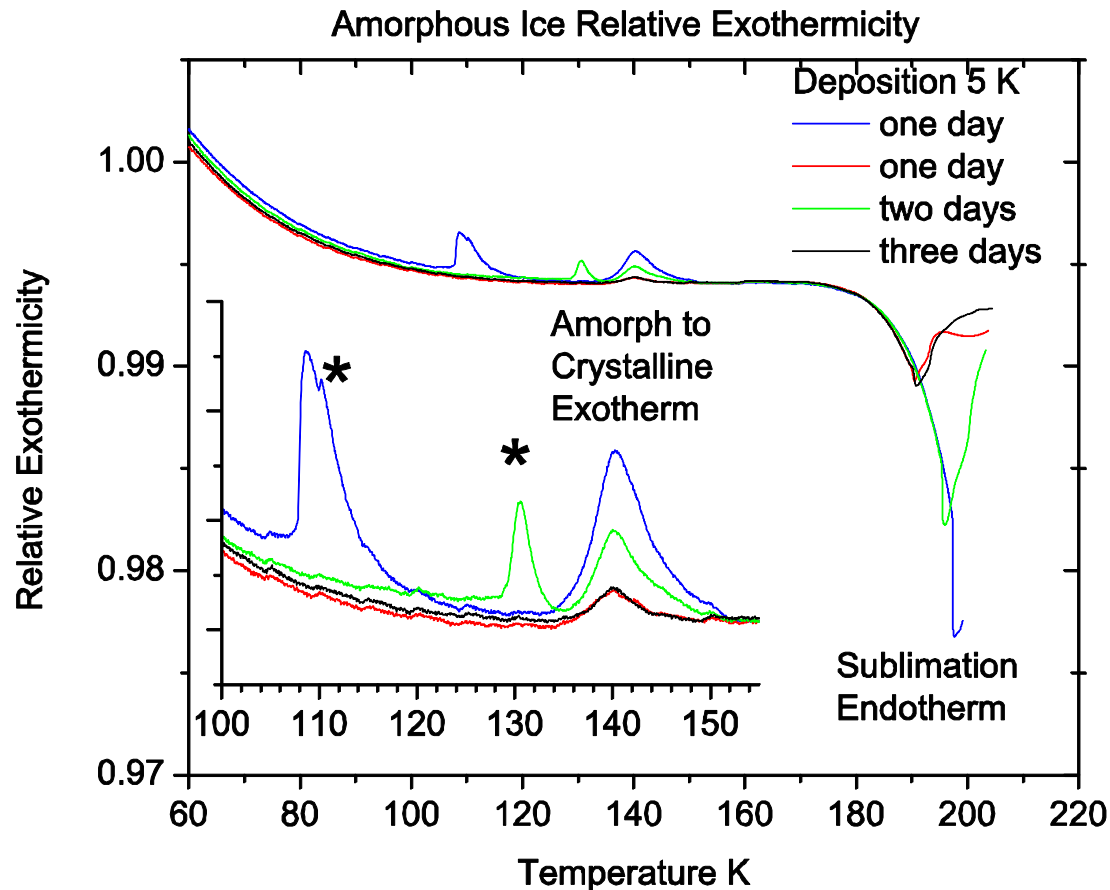
Amorphous Ice Traps Large Amounts of Impurities!

Crystalline Ice Expels Impurities!



Amorphous to Crystalline – Exothermicity

Impurities may change exothermic to endothermic (amorphous to crystalline) transition – to be confirmed in the laboratory



Robert Wagner and Murthy Gudipti (2013)
to be published

Kochi & Sirono GRL 28(2001)827

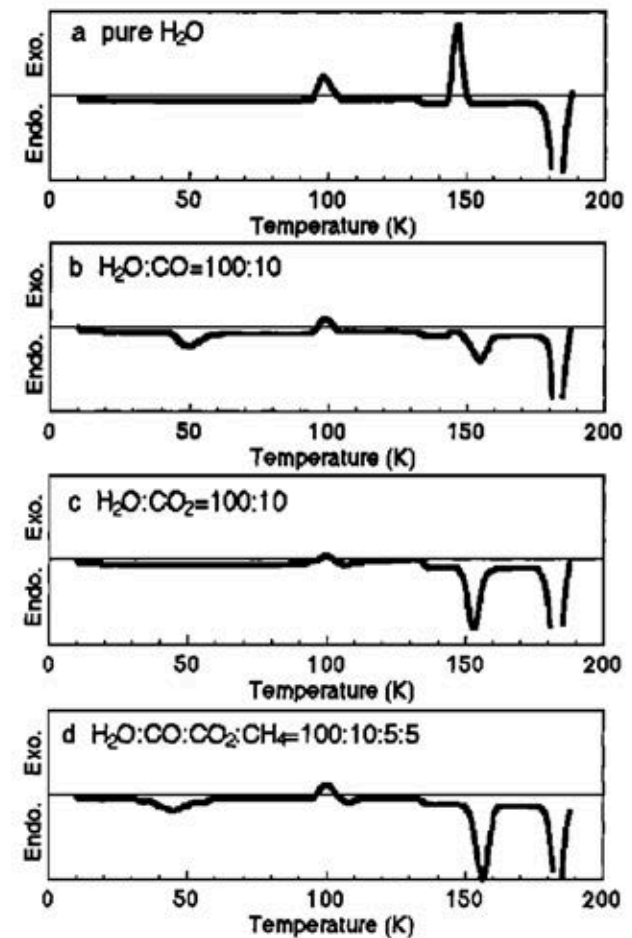
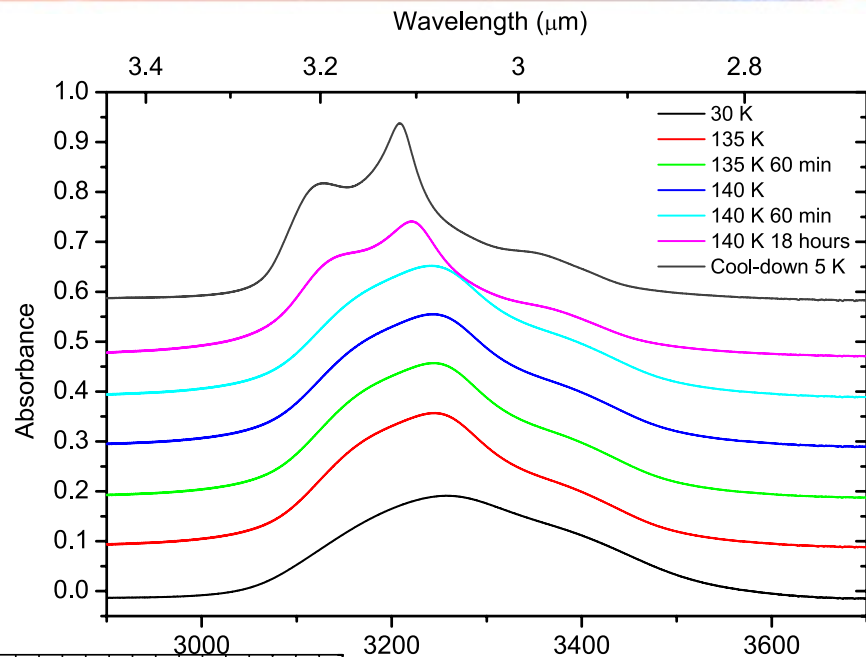
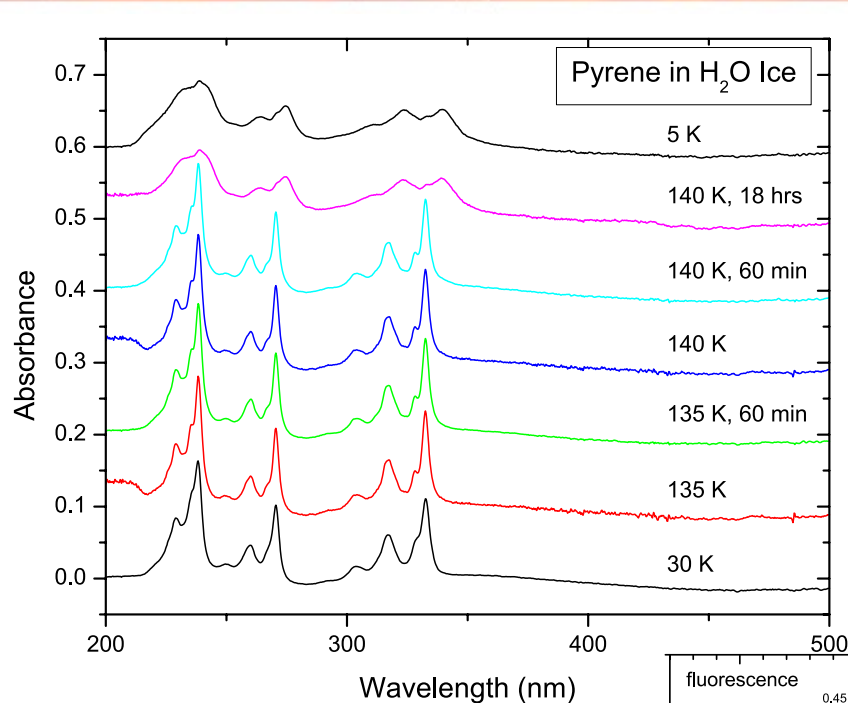


Figure 2. DTA curves of pure (a) and impure (b-d) a- H_2O . Endo., endothermic; Exo., exothermic.



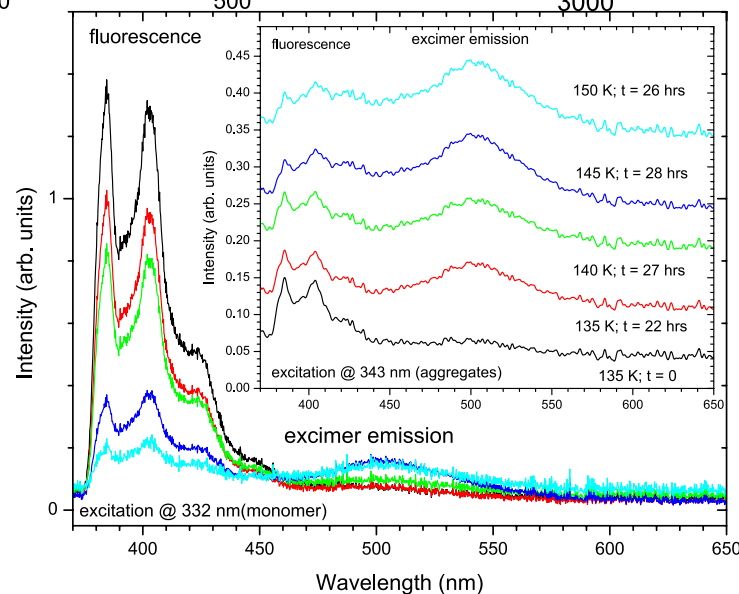
Crystalline Ice NOT a Good Host for Impurities

1:500 Pyrene in H₂O Ice



UV - PAH

Flu - PAH



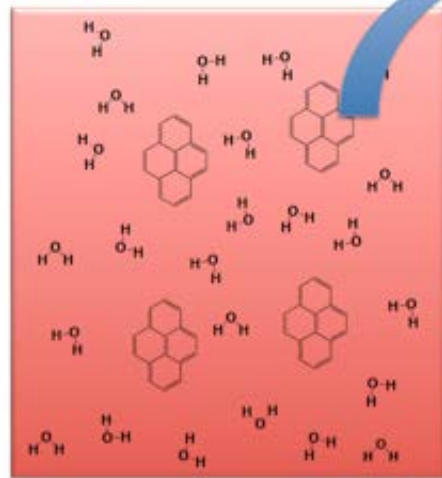
IR - Ice

Lignell & Gudipati
J. Phys. Chem A.
119 (2015) 2607

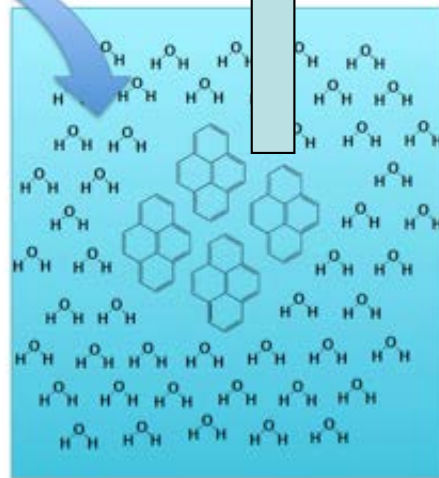
Is there a Crystalline-Ice-Dust-Sintered Mantle?

Phase Transition

Ejection of Impurities

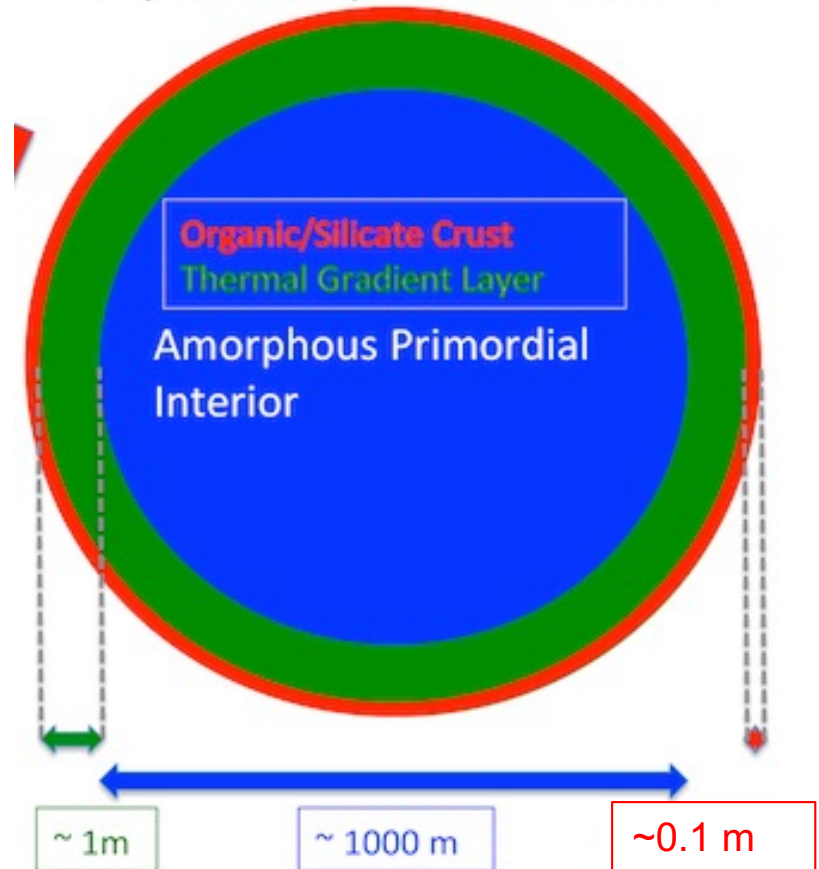


Amorphous Ice



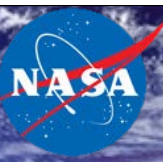
Crystalline Ice

Processed ice ~ 1m
Unprocessed primordial ice >1m



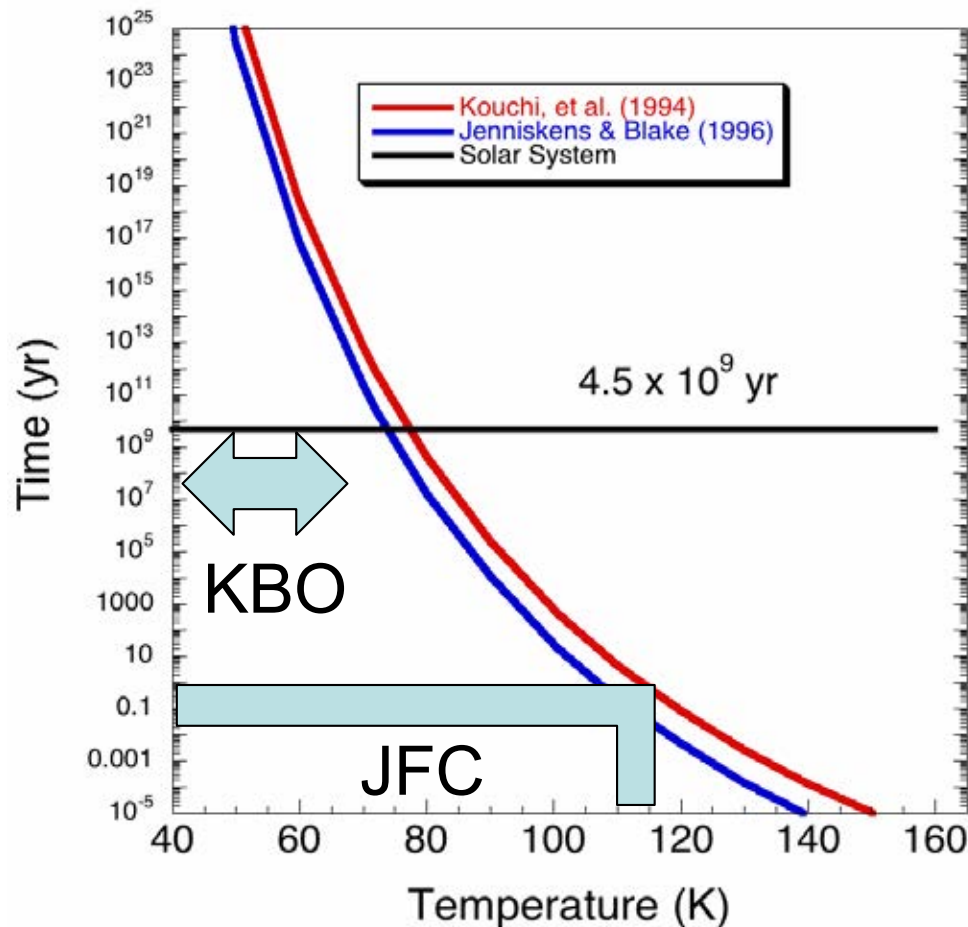
Comet CG/67P

Lignell & Gudipati J. Phys. Chem A. 119 (2015) 2607

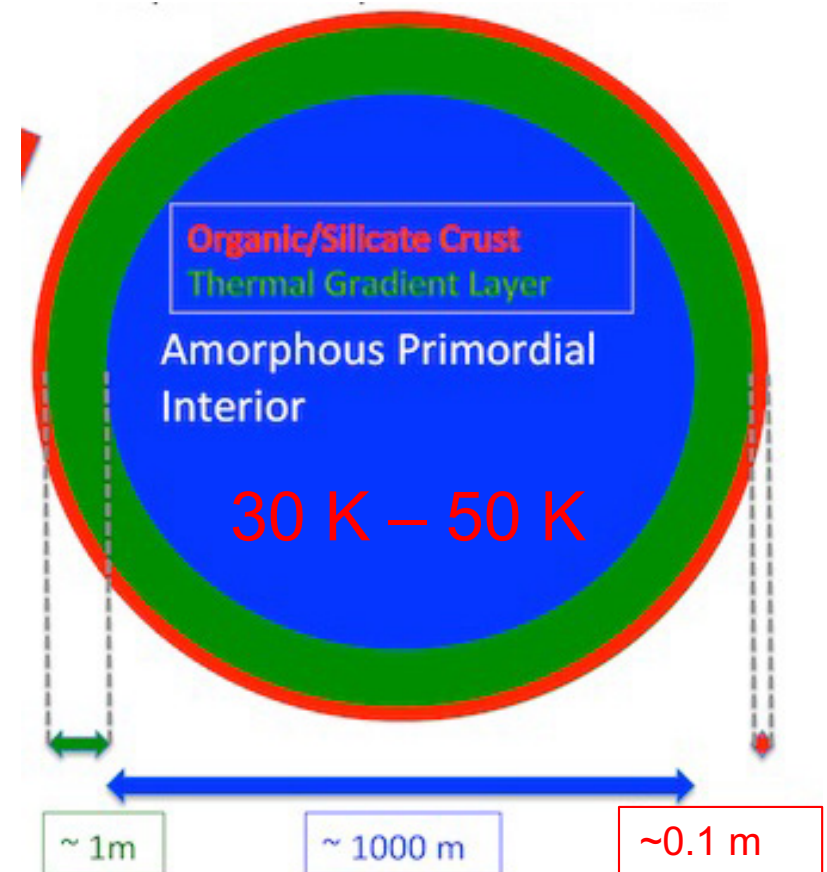


How Primitive is a Comet's Interior?

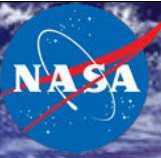
How Thermally Equilibrated are Comets?



Mastrapa, Grundy, Gudipati (Solar System Ices 2013)



Crystalline-ice-Silicate Crust?



Amorphous vs. Crystalline H₂O Ice

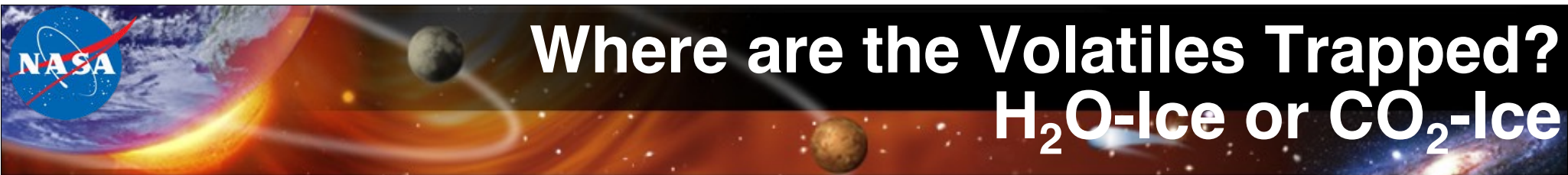
More Laboratory Studies on
Volatile Trapping of Crystalline Ice

It is likely that O₂ and NH₃ bond strongly with H₂O



Trapping of Volatiles in CO₂ Ice

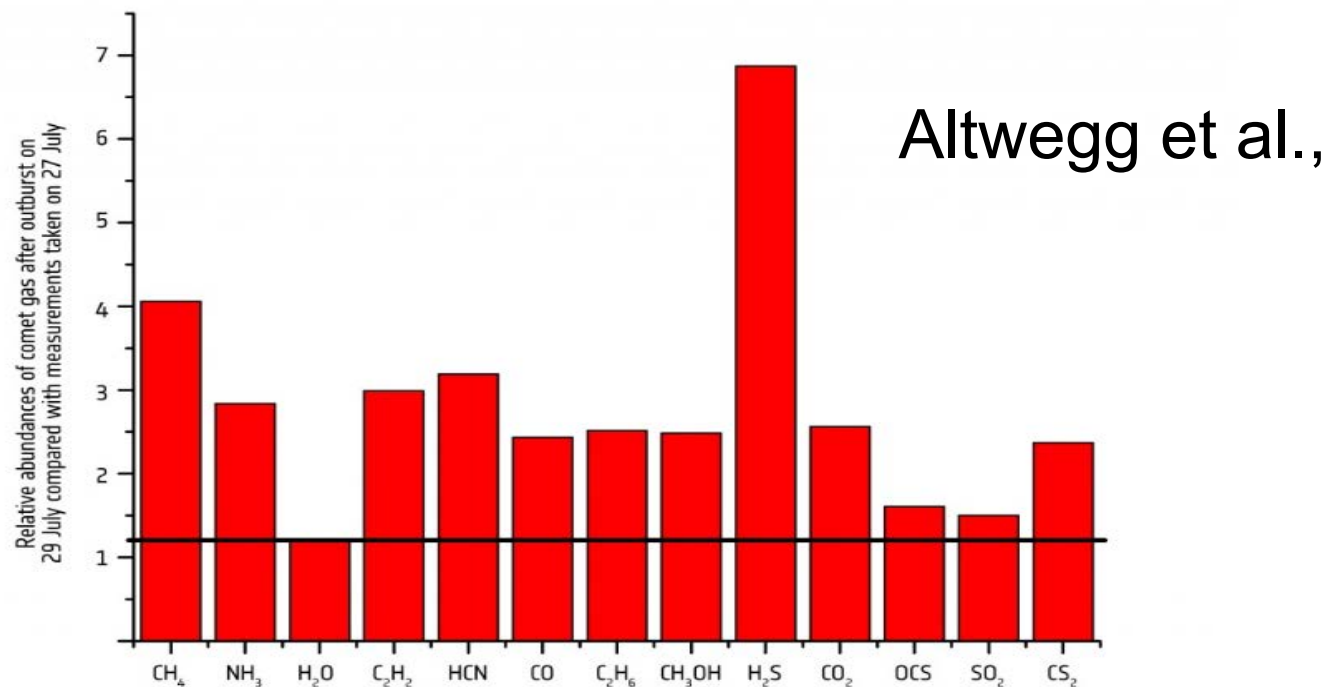
CO₂ is up to 20% of H₂O
Can form Separate CO₂ Ice Domains



Where are the Volatiles Trapped? H₂O-Ice or CO₂-Ice

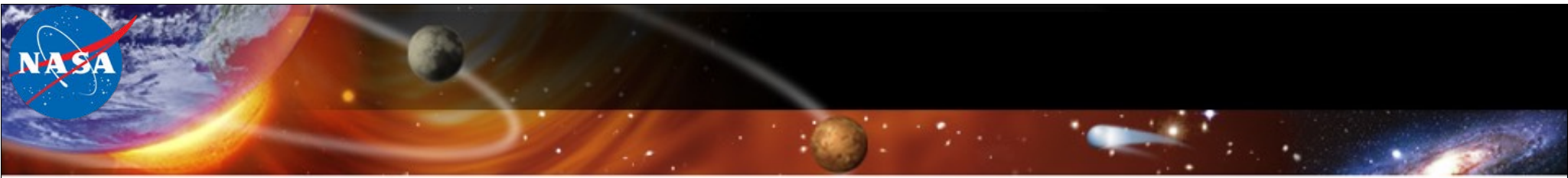
During Outbursts from Interior CO₂ is accompanied by Volatiles

→ ROSINA MEASUREMENTS OF COMET GAS FOLLOWING OUTBURST

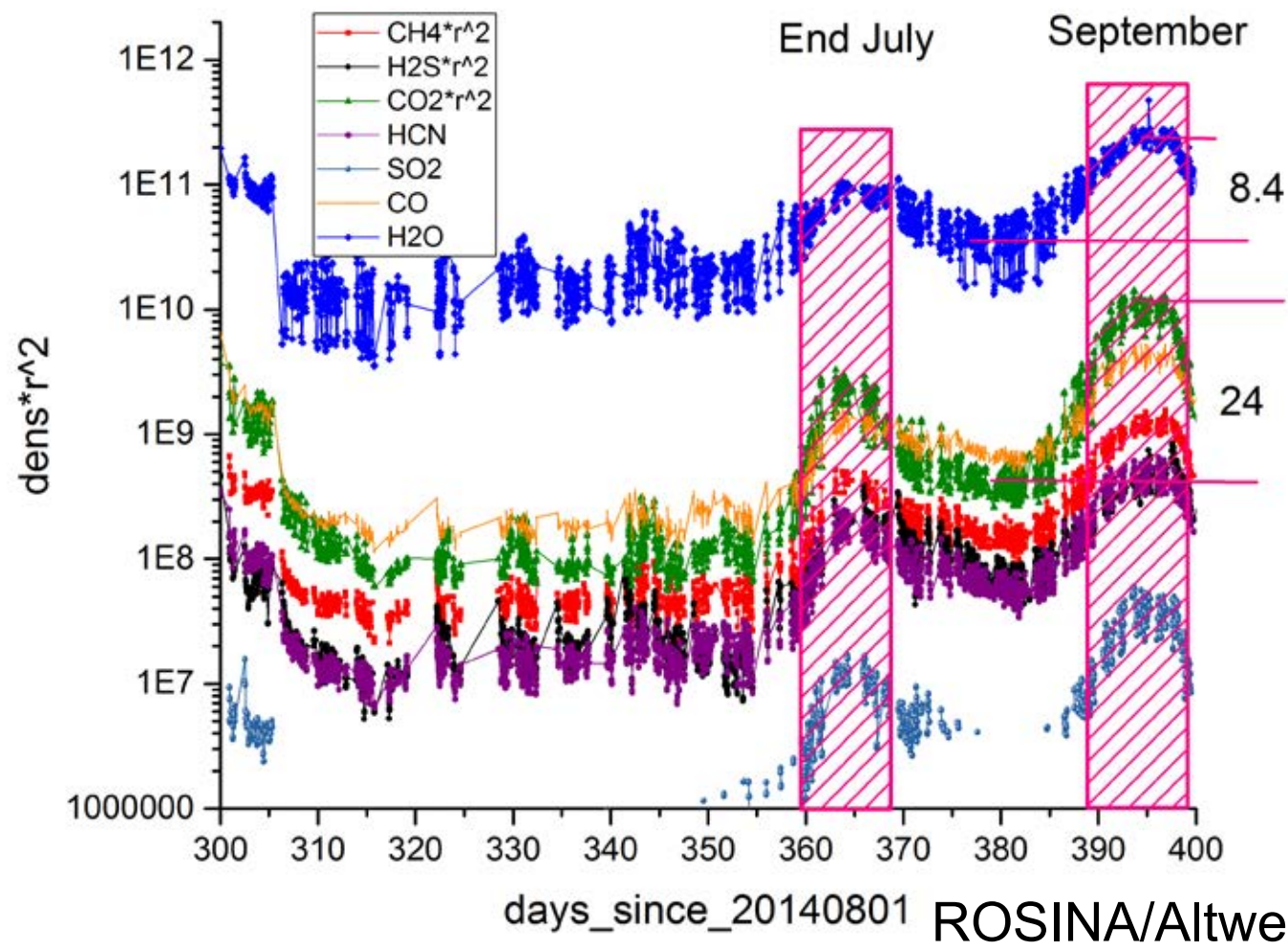


During an outburst of gas and dust from Comet 67P/Churyumov–Gerasimenko on 29 July 2015, Rosetta's ROSINA instrument detected a change in the composition of gases compared with previous days. The graph shows the relative abundances of various gases after the outburst, compared with measurements two days earlier (water vapour is indicated by the black line).

Credits: ESA/Rosetta/ROSINA/UBern/ BIRA/LATMOS/LMM/IRAP/MPS/SwRI/TUB/UMich



Production rates of the volatiles between July and September 2015 increased by a factor 24, water by a factor 8.4. This is most probably also due to the outbursts, which release mostly species more volatile than water.





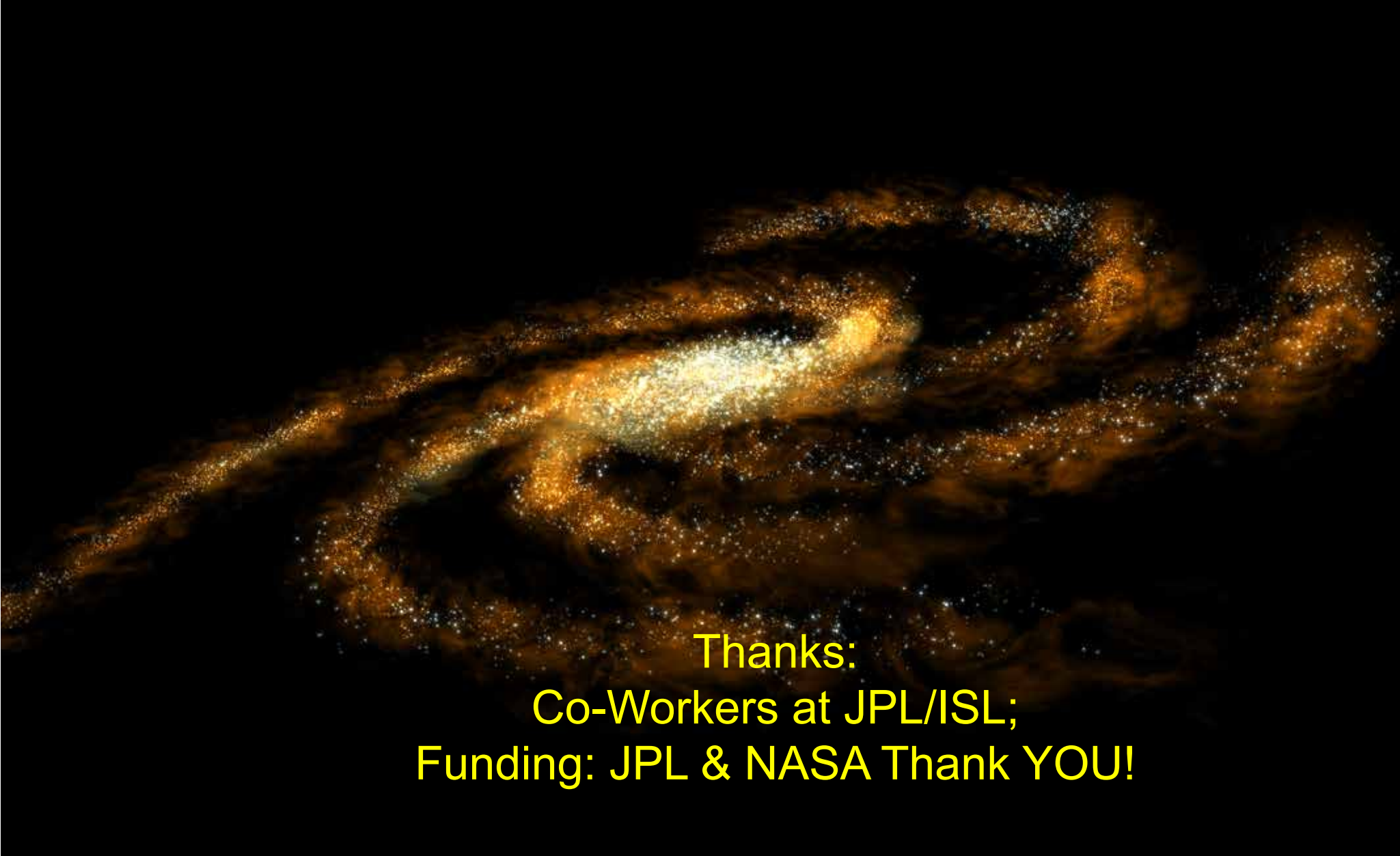
Laboratory Studies Needed

- Exothermicity of Amorphous Water Ice with Impurities
- What is the survivability of Ar, Kr, O₂, N₂, CO, CH₄ (Supervolatiles) – from Pre-Solar to Present Day (10 K – 40 K – 120 K)?
- How/Where are the refractory complex organics produced?
- H₂O ice (amorphous vs. crystalline) and impurities
- CO₂ ice (crystalline) and impurities
- Dust/Ice Simulations at 30 K – 150 K
- How does the interior of a JFC comet work?
Like Pressure Cooker?
- ...

Comet Nucleus Laboratory Research Consortium



Acknowledgments



Thanks:
Co-Workers at JPL/ISL;
Funding: JPL & NASA Thank YOU!